AD/A-002 846

INTEGRAL GLASS COVERS FOR SILICON SOLAR CELLS

GENERAL ELECTRIC COMPANY

PREPARED FOR
AIR FORCE AERO PROPULSION LABORATORY

31 OCTOBER 1974

AD/A-002846

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Space Sciences Laboratory	Unclassified
General Electric Company	2b. GROUP
P. O. Box 8555, Philadelphia, Pa. 19101	

3. REPORT TITLE

INTEGRAL GLASS COVERS FOR SILICON SOLAR CELLS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Technical - May 1971 to October 1974

5. AUTHOR(S) *(First name, middle initial, last name)*

Harry W. Rauch, Sr.
Donald R. Ulrich

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
31 October 1974	70	

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
F33615-71-C-1656	
b. PROJECT NO. 3145	AFAPL-TR-74-14
c. Task No. 19	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. Work Unit No. 31	

10. DISTRIBUTION STATEMENT

Approved for Public Release, Distribution Unlimited

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	AFAPL/POE-2
	Air Force Systems Command
	Wright-Patterson AF Base, Ohio 45433

13. ABSTRACT

A program of inorganic glass development resulting in the formulation of numerous compositions for direct fusion to silicon solar cells was conducted. The glasses were sedimented as -200 mesh particles onto the front surface of the solar cells, then fused, to form an integral cover, at temperatures ranging from $510°C$ to $600°C$ depending on solar cell type and glass composition. Coatings, at least 50 microns thick, were applied to both N/P aluminum - contacted and silver/titanium -contacted cells. Electrical characterization of the bare and coated cells, before and after electron irradiation, shows that some cells can be integrally covered by this technique without degrading their conversion efficiency below an acceptable level. Glass preparation, compositional modifications, and the effect of these changes on fusion temperature, radiation resistance, transmission, and thermal expansion are discussed.

i

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Silicon Solar Cells						
Integral Glass Covers						
Glass Compositions						
Glass Properties						
Transmission						
Radiation Resistance						
Thermal Expansion						
Fusion Temperature						
Radiation Damage to Glasses						

1a

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

AFAPL-TR-74-14

INTEGRAL GLASS COVERS FOR SILICON SOLAR CELLS

Harry W. Rauch, Sr. and Donald R. Ulrich

Approved for public release; distribution unlimited

FOREWORD

This Final Technical Report covers all work under Contract F33615-71-C-1656 from May 19, 1971 to October 31, 1974.

This contract with the Space Sciences Laboratory, General Electric Company, was initiated under Project No. 3145, Task No 19, Work Unit No. 31, "Integral Glass Covers for Silicon Solar Cells."

At the time of submission of this report, the technical efforts were being directed by Lt. John M. Green, AFAPL/POE-2 Energy Conversion Branch, Aerospace Power Division of the Air Force Aero-Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.

The following General Electric Company personnel were contributors to the program in the capacity noted:

T. A. Harris	Transmittance Measurements & Irradiation
R. W. Gunnett	Solar Cell Characterization, Transmittance and Irradiation
L. R. McCreight	Program Manager
R. Peterson	Depth-Dosage Calculations
H. W. Rauch, Sr.	Glass Formulation, Preparation, Evaluation and Solar Cell Application
D. R. Ulrich	Principal Investigator

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

John M. Green, Lieutenant, USAF
Project Engineer/Scientist

FOR THE COMMANDER

Joseph F. Wise, Technical Manager
Solar Energy Conversion
Aerospace Power Division

ii

SUMMARY

The main objective of this program was to develop a stress_free, integral glass cover material and a technique for applying it to large area, hardened solar cell arrays with the expectation that this would reduce the covering costs from approximately $60/watt to $5/watt. The feasibility of meeting this objective was demonstrated.

This objective was approached by formulating glasses, which were applied as very fine particles and fused directly to silicon solar cells. The requisite properties of such glasses include all of the qualities of adhesively bonded covers, namely:

1. High transmission between 0.3 and 1.1 microns

2. Resistance to radiation darkening

3. Moisture resistance

4. Thermal cycle resistance

The glasses must also match the thermal expansion of silicon, and fuse at temperatures which do not degrade cell performance.

More than 100 compositions were formulated, melted, and screened in the development of glasses having the above properties.

iii

Many of the resultant glasses were eliminated during screening because of high fusion temperature, high thermal expansion, or poor radiation resistance. However, about 25 glasses eventually were applied as integral covers to three different types of silicon solar cells. Integral covers, at least 50 microns thick, were fused to both P/N lithium-doped and N/P aluminum-contacted cells and to conventional N/P silver/titanium-contacted cells. I-V response measurements indicated complete power loss in the P/N lithium-doped aluminum-contacted cells, marginal power loss in the N/P aluminum-contacted cells, and essentially no power loss in the silver/titanium-contacted cells.

In addition, modules consisting of nine cells each, in a three-by-three cell symmetry were integrally covered. The cells were joined into modules having 1.0 mil aluminum interconnects which also received a glass coating by virtue of the integral covering technique used.

Two generic types of glass compositions evolved from this program. One consisted of the oxides, $Li_2O \cdot ZnO \cdot B_2O_3 \cdot SiO_2$; the other was composed of $Li_2O \cdot ZnO \cdot B_2O_3 \cdot GeO_2$. Both types also contained Al_2O_3 and Ta_2O_5 as modifier oxides and some of the glasses included CeO_2 or TiO_2 for radiation resistance.

Several of these glasses possess fusion temperatures between 550°-580°C, coefficients of thermal expansion around $6.0 \times 10^{-6}/^\circ$C, and good transmission, before and after electron irradiation. It is difficult, therefore, to select a single composition as the best integral cover material. Since HR-126G has

been applied to more than 25 N/P silver/titanium-contacted cells, this glass becomes the leading candidate. However, acceptable I-V response data were also obtained from cells covered with HR-12B4, GE-101673 and GE-122673.

ABSTRACT

A program of inorganic glass development resulting in the formulation of numerous compositions for direct fusion to silicon solar cells was conducted. The glasses were sedimented as -200 mesh particles onto the front surface of the solar cells, then fused, to form an integral cover, at temperatures ranging from $510^{\circ}C$ to $600^{\circ}C$ depending on solar cell type and glass composition. Coatings, at least 50 microns thick, were applied to both N/P aluminum - contacted and silver/ titanium - contacted cells. Electrical characterization of the bare and coated cells, before and after electron irradiation, shows that some cells can be integrally covered by this technique without degrading their conversion efficiency below an acceptable level. Glass preparation, compositional modifications, and the effect of these changes on fusion temperature, radiation resistance, transmission, and thermal expansion are discussed.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I. INTRODUCTION

The need to protect silicon solar cells from natural and man-made radiation and from micrometeorite damage has been well established. However, the most satisfactory technique for achieving this protection has not been identified. The most commonly used method is to bond a thin (6-10 mil) sheet of fused silica to the cell surface with an organic adhesive. This technique is not completely satisfactory because radiation eventually degrades the adhesive sufficiently to impair cell output. This reason together with the economics of adhesively bonded covers has focused much attention on the development of integral covers for solar cells.

II. CONVENTIONAL COVER GLASSING APPROACH

A. General Description

To date, all flight solar array designs have utilized discrete cover glasses which are bonded to the solar cell active surface with a clear silicone adhesive. Either silica or a high silica, i.e. Corning 0211 microsheet or 7940 fused silica cover glass material are conventionally used, usually with a blue or blue-red reflecting filter on the solar cell facing surface. The outside facing surface is covered with an anti-reflection coating. The blue reflecting filter system is used on contemporary solar array designs and provides a transmission cut-on wavelength of about 0.4 microns. This cut-on was established to protect the clear silicone cover glass adhesive against the darkening effects of transmitted ultraviolet radiation.

B. Material Cost

The cover glass unit cost varies with quantity, material, thickness, size, filter system, dimensional tolerance and mechanical imperfections. The effect of some of these variables on cover glass material cost is shown in Figures 1 through 3 [1,2]*. Figure 1 shows the price variation due to the type of coatings applied to the glass substrate. This data reflects 1967-69 prices and is adjusted to a baseline (zero-cost) which corresponds to an AR coating plus a blue reflecting filter. Figure 2 shows the relative cost of fused silica cover glass (2 x 4 cm, with blue reflecting filter and AR coating) as a function of glass thickness. The optimum thickness for fused silica covers is about 500 microns (20 mils). The effect of quantity on cost for a blue filtered, AR coated cover glass is shown in Figure 3. If the filter configuration is changed to either AR only or AR plus blue-red, the values in Figure 1 must be added to the values in Figure 3. The influence of dimensional tolerance is reflected by a 5 to 10 percent increase in price if the typical tolerances of $\pm$ 75 microns ($\pm$ 0.003 inch) on length and width and $\pm$ 25 microns ($\pm$ 0.001 inch) on thickness are tightened. Similarly, a tightening of nominal edge and corner chip specifications will cause another 5 percent increase in unit cover glass price.

C. Installation Cost

The cover glass installation cost is a function of the cover-to-cell location tolerances, cover glass size and thickness, type of adhesive used, and quantity. Figure 4 shows the approximate range of cover glass installation

---

* Numbers in parenthesis are references cited in Section X. In addition, a Bibliography of selected reading is included in Section XI.
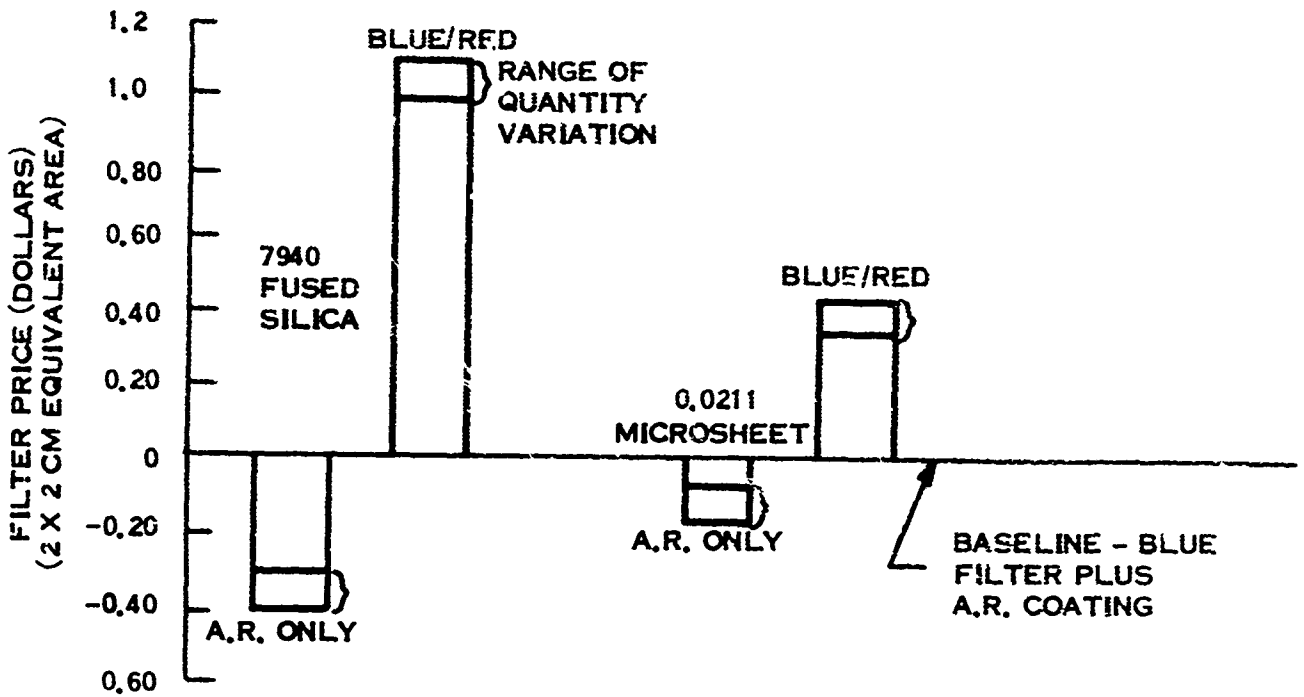
Figure 1. Price of various filter types on solar cell covers
(Reference 1)
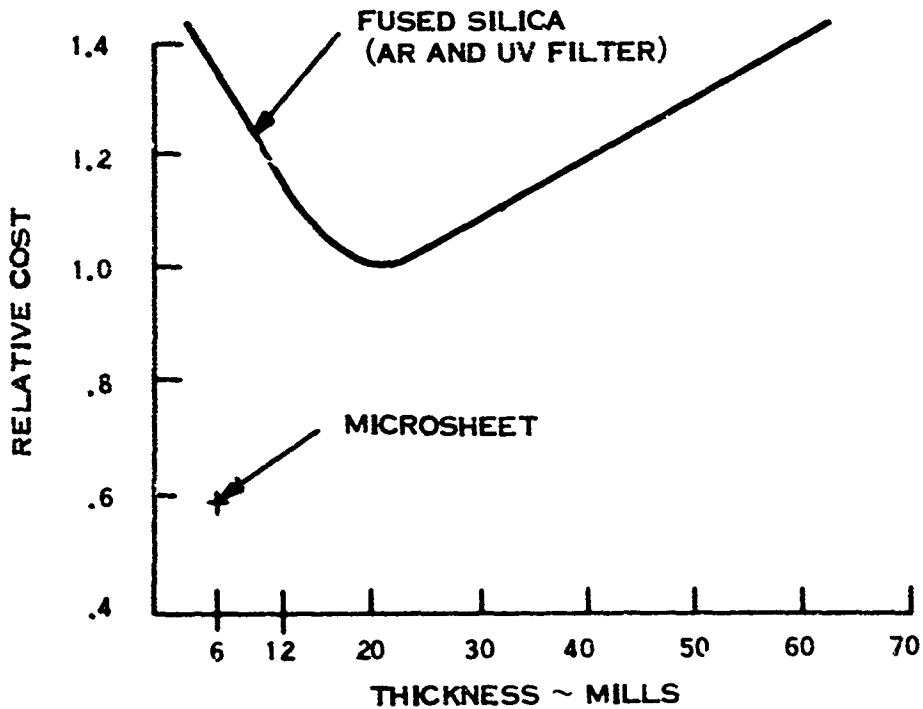
Figure 2. Relative cost versus thickness for 8 cm^2 coverglasses
(Reference 2)

3
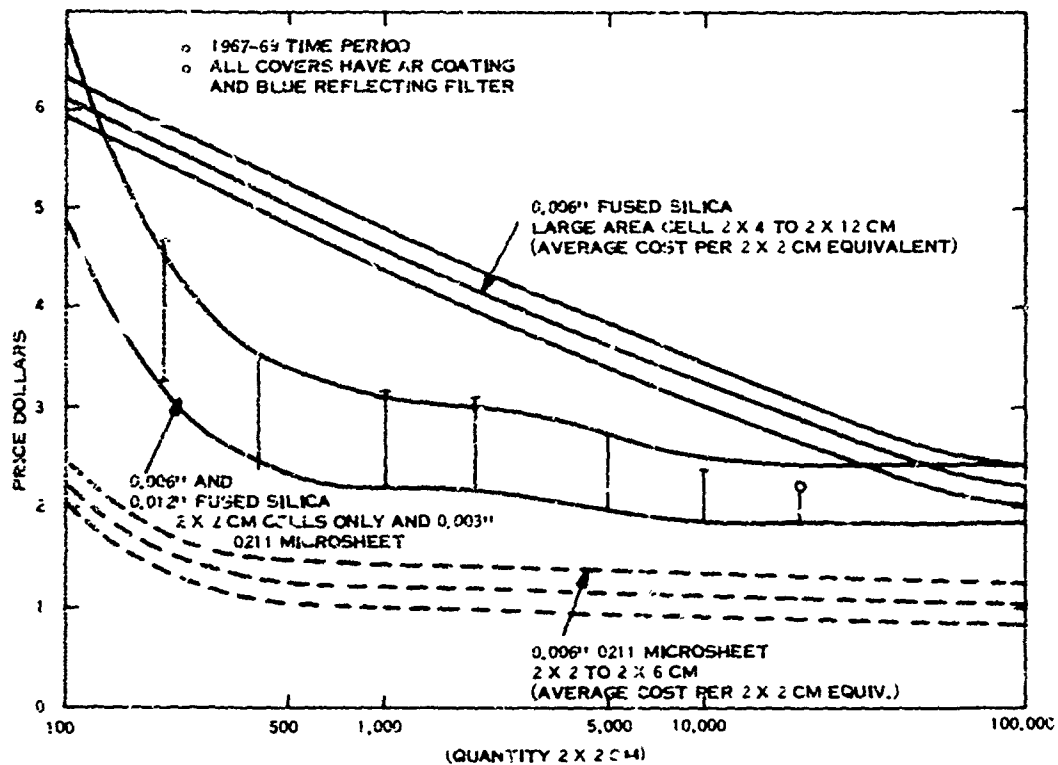
Figure 3. Solar cell coverglass price versus quantity
(Reference 1)

● 1 – 0.003" MICROSHEET
● 2 – 0.006" MICROSHEET OR SILICA
● 3 – 0.006" 2 X 6 CM
● 4 – 0.012" MICROSHEET OR SILICA
● 5 – 0.006" 2 X 6 CM
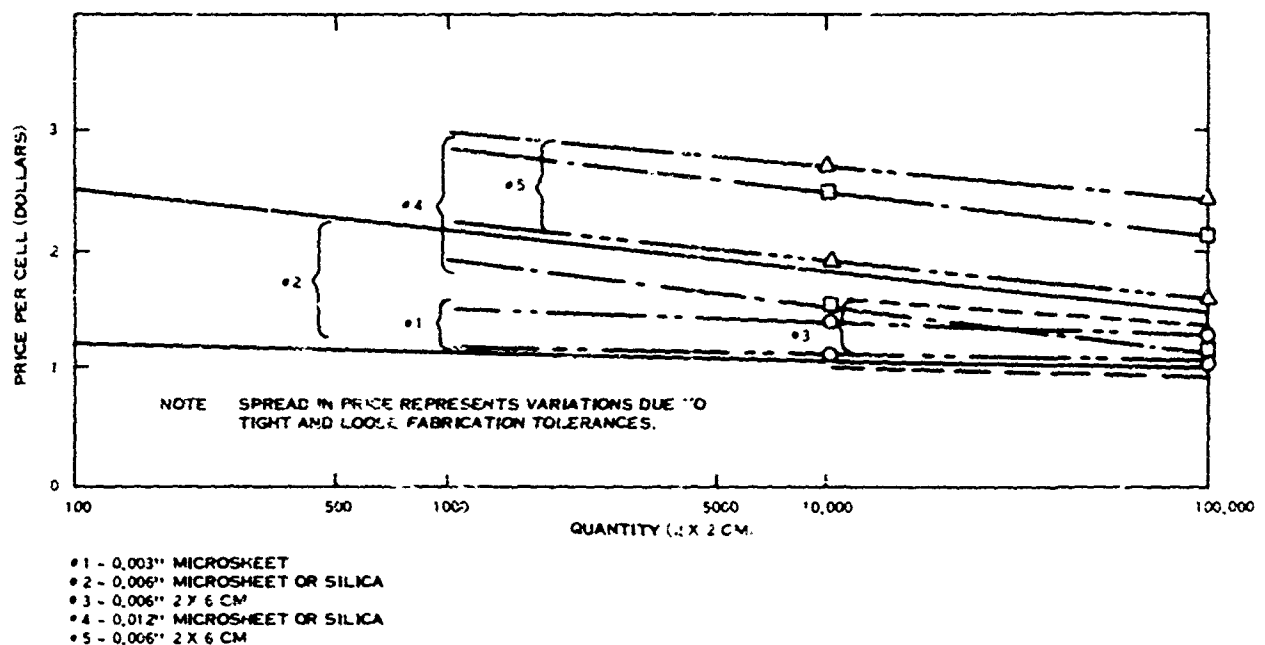
Figure 4. Installation price of various types of solar cell covers versus quantity
(Reference 1)

4

prices for various cover glass thickness as a function of the quantity installed. These curves are based on prevailing prices for the period 1967-69, and include typical burdened labor and a normal breakage allowance. The upper curve for each type represents the more difficult and costly approach with tight cover glass tolerances, rigid ("zero-gap") cover placement tolerances, and the most costly adhesive (R63-489). The lower curve represents loose cover glass dimensions, more liberal placement tolerances and the easily applied RTV602 adhesive.

Table 1 summarizes the total cover glassing cost analysis for a glass thickness of 150 microns (6 mils). These data are derived by the following steps:

a. Determine the coating cost correction from Figure 1

b. Determine the upper and lower price for each material type from Figure 3

c. Determine the upper and lower price for tight and relaxed specifications for installation from Figure 4.

Table I: Price Comparison of Conventionally Covered Solar Cells
(Reference 1)

Cover Material	0.006" 7940 Fused Silica 50,000 PCS				0.006" 0211 Microsheet 50,000 PCS			
Cover and Installation Specifications	Tight		Relaxed		Tight		Relaxed	
Coating on Cover	A.R. Only	A.R. and Blue	A.R. Only	A.R. and Blue	A.R. Only	A.R. and Blue	A.R. Only	A.R. and Blue
Coating Cost Change	-0.42	0	-0.42	0	-0.17	0	-0.17	0
Cover Cost	2.50	2.40	1.73	1.83	1.32	1.25	0.67	1.85
Installation Cost	1.60	1.60	1.00	1.00	1.60	1.60	1.00	1.00
Total Cost	3.68	4.00	2.31	2.83	2.75	2.85	1.50	1.85

6

III. INTEGRAL COVER GLASSING APPROACH

The development of an integral solar cell cover is an attractive objective. Organic adhesives with their attendant shortcomings would be eliminated and possibly the need for anti-reflection coatings could be minimized. Finally, integral covers should have a decided economic advantage since the tedious labor of cover slide/cell assembly would be eliminated.

The use of integral glass coatings to protect silicon surfaces has been studied by numerous investigators for nearly two decades. Techniques such as reactive, high vacuum ion beam, and rf sputtering, electron beam deposition, chemical vapor deposition, and thermal decomposition have been employed to deposit fused silica, alumino-silicates, aluminoborosilicates, borosilicates, phosphosilicates and other glasses onto silicon. However, a serious limitation inherent to these techniques is the introduction of sufficient residual stress into the cell to impair its conversion efficiency. Only recently has a possible solution to this problem been reported [3]. Another major disadvantage of all these methods is the very slow rate of coating deposition.

The coating technique we used throughout our study is similar to porcelain enamelling. It consists essentially of depositing a layer of very fine glass particles onto a solar cell and by subsequent thermal treatment, fusing the particles together and to the cell surface. This technique has been previously described [4] to apply borosilicate glasses to doped silicon

slices and by several additional processing steps, produce an integrally

coated solar cell. However, the temperature required to fuse borosilicate

glasses to either silver/titanium or aluminum contacted solar cells would

completely degrade the cells. Therefore, we have concentrated on developing

a series of glasses specifically for application to silicon solar cells keeping

in mind the required low fusion temperature, low thermal expansion, high

transmittance, good radiation resistance, and chemical durability.

IV. GLASS DEVELOPMENT

A. Background

In August 1968 a program was initiated in our laboratory to develop

a glass which could be directly fused to silicon. One of the resulting

compositions, an alkali borogermanosilicate, showed considerable promise.

Pieces of this glass, about 30 mils thick were fused, at $850^{\circ}C$, to a 30 mil

thick silicon wafer. After the wafer cooled to room temperature, it was

immersed in liquid nitrogen ($-196^{\circ}C$) with no apparent thermal shock damage

to the glass. In addition, an 80 mil thick disk of this glass was exposed to

50 Mrad of Sr^{90} beta irradiation with no effect on transmission, which

exceeded 80% from 0.6 to 1.1 microns.

Our early work ultimately led to the initiation of this program with,

however, a very much more difficult objective; the development of glasses

and a technique for applying them to aluminum-contacted silicon solar cells.

8

The application of glass by the fusion technique to aluminum-contacted silicon solar cells involves a severe temperature limitation because of the $577^\circ C$ eutectic which exists in the aluminum-silicon system. Initial feasibility for achieving this objective was demonstrated late in 1969 with the development of a zinc oxide-modified alkali silicogermanoborate glass. Smooth, craze-free, integral films of this glass at least 50 microns thick were produced on 30 mil thick silicon wafers using a fusion cycle of $565^\circ C/5$ minutes. Storage of these coated silicon wafers in our laboratory for 18 months did not alter the integrity of the glass films. This behavior prompted our selection of the glass as the parent composition for developing a stress-free integral cover for silicon solar cells according to the objectives of this program. However, the glass darkened considerably when exposed to about 60 Mrads of Sr^{90} beta irradiation and crazed badly when applied in films thicker than 75 microns. We therefore concentrated on compositional adjustments to correct these deficiencies.

Raw materials consisting of single and double oxide, carbonates, phosphates, and fluorides were carefully weighed, thoroughly mixed and placed into platinum crucibles. The batches, calculated to yield 50 grams of glass, were melted in an electric furnace at selected temperatures in the range of 1000 to $1350^\circ C$, depending on composition.

Each glass was melted, quenched, and re-melted, before specimens were made for thermal expansion, fusion, and transmittance evaluation. Initially all the melts were water quenched, but later quenching consisted

of pouring the melt through rotating steel rolls. This technique produces ribbon about 14 mils thick which serves very well as fusion and transmittance evaluation specimens. Thermal expansion was measured on bars about 1/4" x 1/4" x 2" which are made by pouring molten glass into a graphite mold having two cavities of approximately those dimensions. The bars were annealed at times and temperatures dependent on composition. A typical annealing schedule was $500^{\circ}C/2$ hours.

B. Parent Glass Modification

The parent glass was initially modified by a series of compositional adjustments as follows:

To lower the thermal expansion

ZnO content increased
K_2O replaced with Na_2O
Additions of Al_2O_3, HfO_2, La_2O_3, and Ta_2O_5

To improve the fusion behavior

GeO_2 content increased
Additions of PbO and La_2O_3

To improve the moisture resistance

B_2O_3 content decreased
Additions of Al_2O_3 and La_2O_3

To improve the radiation resistance

Gradual replacement of GeO_2 with SiO_2
Addition of CeO_2

The most significant result of these adjustments was the development of two very radiation resistant glasses, 1TL and 1TLH. Figures 5 and 6 show that the transmission of both glasses remained essentially unchanged after a 24 hour exposure to 0.6 MeV beta irradiation. ($\sim 10^{15}$ e/cm^2 fluence). Most silicate glasses discolor as a result of exposure to high energy radiation in proportion to their alkali content, but both of these glasses contain in excess of 16.0 weight percent Li_2O. Undoubtedly their ceria contents are related to their very good radiation resistance, but this does not totally provide an explanation. Many glasses having identical ceria contents were made before and after these two without exhibiting the same very good radiation resistance. Unfortunately, both of those glasses had very high coefficients of thermal expansion ($\sim 12 \times 10^{-6}/^{\circ}C$) which eliminated them as candidate materials for integral covers. In fact, none of the glasses resulting from this first series of compositional adjustments had thermal expansion coefficients as low as that of the parent composition ($9.7 \times 10^{-6}/^{\circ}C$).

Some general observations regarding the initial modifications follow:

ZnO contents greater than about 16.0 weight percent produce opacity

Replacement of GeO_2 with SiO_2 increases the fusion temperature but does not improve the radiation resistance

Reducing the B_2O_3 content and adding Al_2O_3 or La_2O_3 improves the moisture resistance

Addition of ceria significantly improves the radiation resistance.
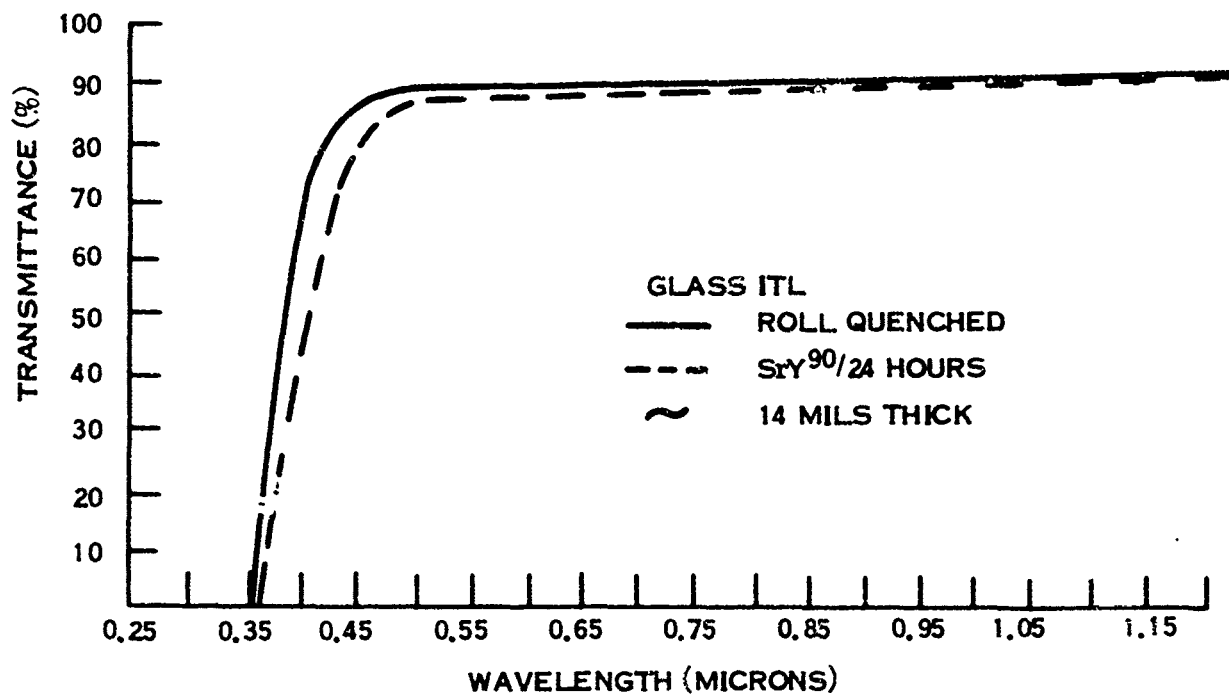
Figure 5. Transmission profiles of glass No. 1TL before and after electron irradiation
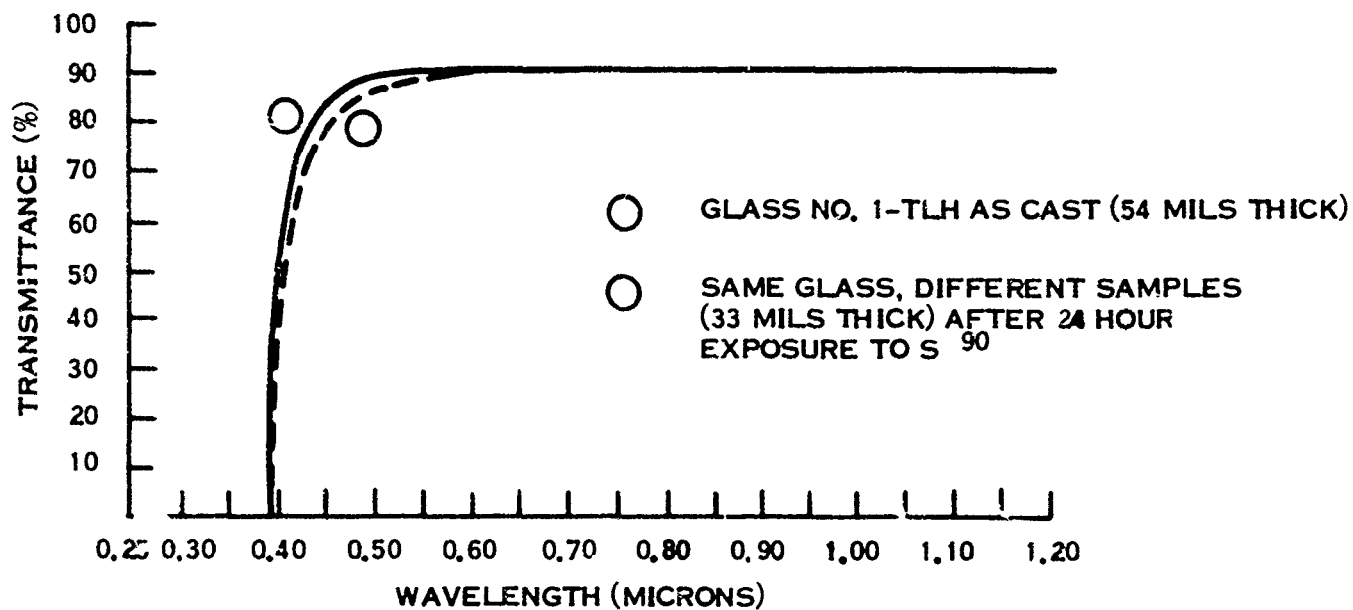
Figure 6. Transmission profiles of glass No. 1TLH before and after electron irradiation

12

Representative compositions in oxide weight percent of glasses in this series are shown in Table 2.

C. Fluoride-Modified Glasses

Fluoride additions to oxide glasses reportedly can reduce the viscosity and lower the softening temperature[5-8], and fluoroberyllate and phospho-fluoride glasses have been reported to be highly ultraviolet transmitting[9, 10]. Several base compositions, such as Nos. 19 and 22 were modified with partial or complete substitution of LiF for Li_2O, KF for K_2O, NaF for Na_2O, ZnF_2 for ZnO and AlF_3 for Al_2O_3.

The introduction of fluorides into some of the glasses we developed increased the fluidity with a corresponding reduction in the softening temperature. For example, the complete replacement of Li_2O and ZnO by LiF and ZnF_2 in glass No. 22 lowered the softening temperature from $500^{\circ}C$ to $463^{\circ}C$ as determined by differential thermal analysis. However, electron irradiation darkened the glasses even when they contained ceria. For this reason further work was terminated.

TABLE II. COMPOSITION IN OXIDE WEIGHT PERCENT OF REPRESENTATIVE GLASSES IN FIRST SERIES

	1	1C	1L	1TL	1TLH	1TLN	7	9	11	19	24 B8
K_2O	6.5	6.5	6.5	-	-	-	-	-	-	-	-
Li_2O	6.2	6.2	6.2	17.0	16.5	11.5	6.2	4.0	8.1	10.7	11.3
Na_2O	-	-	-	-	-	9.5	-	-	-	-	12.2
ZnO	11.3	11.3	11.2	6.6	6.4	6.3	11.2	21.5	5.5	-	6.7
Al_2O_3	-	-	-	-	-	-	7.0	6.7	6.9	10.1	16.8
B_2O_3	38.6	38.3	38.2	22.5	21.8	21.4	38.4	27.6	28.2	37.6	22.9
La_2O_3	-	-	0.9	10.5	10.2	10.0	-	-	-	-	-
Ta_2O_5	-	-	-	7.1	6.9	6.8	-	-	-	-	-
CeO_2	-	0.5	-	0.5	1.4	0.5	-	1.1	0.7	0.5	0.8
GeO_2	29.0	28.9	28.8	-	-	-	28.8	27.6	42.5	36.9	-
HfO_2	-	-	-	-	3.3	-	-	-	-	-	-
SiO_2	8.4	8.3	8.3	35.7	33.4	34.0	8.3	11.5	8.1	4.3	29.3

14

D. Phosphorous Pentoxide-Containing Glasses

The very low surface tension of molten P_2O_5 [11] and its ability to impart high ultraviolet transmission to glass [12] suggested the use of this oxide as a glass constituent. Sixteen compositions were formulated and melted in which the P_2O_5 content was varied from 6.0 to 27.9 weight percent. Neither the fusion behavior nor the ultraviolet transmission of these glasses were improved over those glasses which did not contain P_2O_5. In addition, several of the glasses became dense opals while still in the molten state, several became dense opals during the re-heat of fusion evaluation, and others became lightly opalescent during fusion evaluation. For these reasons, the use of P_2O_5 as a glass constituent was discontinued.

E. Bismuth Oxide-Containing Glasses

Bismuth oxide compositions based on the low temperature binary eutectics $Li_2O \cdot Bi_2O_3$ and $B_2O_3 \cdot Bi_2O_3$ were investigated for their potential to reduce fusion temperatures. In the eutectic ratios, a glass consisting of Li_2O, Na_2O_3, ZnO, Al_2O_3, B_2O_3, Bi_2O_3, La_2O_3, SiO_2, GeO_2 and CeO_2 in the amounts of 2.1, 1.0, 5.0, 10.0, 25.0, 16.1, 5.0, 29.7, 5.0 and 0.3 percent, respectively, was developed. Samples of this glasses which varied in thickness from 33 to 55 mils strongly adhered when fused to silicon at $490^{\circ}C$ for 20 minutes. Several large crack free areas were observed. One mil samples applied to N/P silver/titanium-contacted cells by the frit and fusion technique did not show evidence of microcracks or crazing.

15

The pre-irradiation curve of a 35 mil sample showed a cutoff at 0.4 microns and a transmittance of 85 percent at 0.5 microns. There was little change in the pre-irradiation curve after exposure to the SrY^{90} source. However, because of the 0.4 micron cutoff, further work was not pursued.

F. Lead Oxide-Containing Glasses

A continuing goal of the glass development studies was reduction of the fusion temperature without detrimentally affecting the other required properties. Consequently, lead oxide, having a well established reputation for fluxing ability, was incorporated into a series of glasses. It was hypothesized that the position of PbO in the glass network structure may have beneficial fusion effects in small percentages. These compositions consisted essentially of $B_2O_3 \cdot SiO_2$ or $B_2O_3 \cdot GeO_2$, to which additions of Li_2O, PbO, ZnO, Al_2O_3, La_2O_3, Ta_2O_5 and CeO_2 were made. Representative compositions in oxide weight percent are tabulated in Table 3. However, the fusion behavior of these glasses was not significantly improved and the high atomic number of lead could be detrimental to hardenability. Therefore, subsequent glass development excluded lead oxide as a batch constituent.

G. Final Series – $Li_2O \cdot ZnO \cdot B_2O_3 \cdot SiO_2$ and $Li_2O \cdot ZnO \cdot B_2O_3 \cdot GeO_2$ Glasses

The final series of modifications was based on the oxide systems, $Li_2O \cdot ZnO \cdot B_2O_3 \cdot SiO_2$ and $Li_2O \cdot ZnO \cdot B_2O_3 \cdot GeO_2$, to which additions of Al_2O_3, La_2O_3, Ta_2O_5, CeO_2 and TiO_2 were made. Melts of these general types consistently yielded glasses having relatively low thermal expansion and fusion temperature, good radiation resistance and high transmission. Compositions,

16

TABLE III. COMPOSITION IN WEIGHT PERCENT OF LEAD-OXIDE CONTAINING GLASSES

Oxide	HR - SERIES						GE - SERIES					
	16A	16B	16C	16D	16E	16F	1	2	3	4	5	6
Li_2O	4.0	4.0	4.0	4.0	4.0	4.0	5.0	5.0	5.0	-	5.0	5.0
PbO	3.0	3.0	4.0	4.0	3.0	3.0	10.0	10.0	-	5.0	5.0	5.0
ZnO	2.0	2.0	1.0	1.0	2.0	2.0	5.0	5.0	5.0	5.0	5.0	5.0
Al_2O_3	2.0	2.0	2.0	2.0	2.0	2.0	5.0	5.0	5.0	5.0	5.0	3.0
B_2O_3	68.0	68.0	68.0	68.0	68.0	68.0	60.0	60.0	70.0	70.0	60.0	62.0
Ta_2O_5	5.0	5.0	5.0	5.0	5.0	5.0	-	-	-	-	4.8	4.8
CeO_2	0.2	0.2	0.2	0.2	-	-	-	-	-	-	0.2	0.2
GeO_2	10.8	15.8	10.8	15.8	16.0	11.0	15.0	-	15.0	15.0	15.0	15.0
SiO_2	5.0	-	5.0	-	-	5.0	-	15.0	-	-	-	-

Oxide	GE-5973 SERIES							
	1	2	3	4	5	6	7	8
Li_2O	-	-	2.0	2.0	2.0	2.0	2.0	2.0
PbO	5.0	5.0	3.0	3.0	3.0	3.0	3.0	3.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	10.5	3.0
Al_2O_3	-	5.0	5.0	5.0	5.0	10.0	5.0	5.0
B_2O_3	70.0	70.0	70.0	70.0	70.0	65.0	60.0	65.0
Ta_2O_5	-	-	-	-	-	-	5.8	-
CeO_2	-	-	-	-	-	-	0.2	-
GeO_2	-	-	-	15.0	10.0	-	14.0	15.0
SiO_2	20.0	15.0	15.0	-	5.0	15.0	-	-

selected to represent the development trend in this series, are shown in Table 4. Throughout this series an attempt was made, with few exceptions, to keep the Li_2O content at, or below, 5.0 weight percent, to maintain the combined ZnO, Al_2O_3, La_2O_3 and Ta_2O_5 content between 10.0 and 25.0 weight percent, to add either CeO_2 or TiO_2 in amounts of 0.5 weight percent orders, and use B_2O_3, SiO_2 and/or GeO_2 to complete the remainder of the compositions.

H. Fusion Evaluation

This property was evaluated by two methods. One involved the preparation of a slurry consisting of -200 mesh particles of glass in an organic liquid. Amyl acetate/ethocel mixtures, various alcohols, and alcohol/ethyl acetate mixtures were used as the slurry vehicle. The surface of a 13 mil thick silicon wafer was partially covered with glass particles deposited from the slurry. The film was dried, and the coated wafer was then heated at the lowest temperature which caused the glass particles to fuse to each other and bond to the silicon. The other method consisted of placing a small piece ($\sim$ 1/4" x 1/4" x 0.014") of roll quenched glass on the silicon wafer and heating as previously described.

The wetting and bonding to silicon, as well as a very qualitative analysis of glass/silicon thermal expansion match, was obtained by these techniques.

18

TABLE IV. COMPOSITION IN WEIGHT PERCENT OF SELECTED GLASSES FROM FINAL MODIFICATIONS

HR - SERIES

Oxide	t	8A	8C	9	9C	9H	10	10A	12	12B	12BG	12B 4	12BG 2	13 C	13 L'
Li_2O	12.7	15.0	15.0	5.0	5.0	5.0	5.0	5.0	5.0	5.2	5.2	3.0	5.2	5.2	4.5
ZnO	11.3	6.0	6.0	5.0	6.5	10.0	5.0	5.0	5.0	5.0	5.0	6.0	5.0	3.0	4.5
Al_2O_3	-	22.0	2.0	2.5	1.0	2.5	-	1.0	2.0	1.0	1.0	5.0	1.0	3.0	2.0
B_2O_3	38.6	70.0	70.0	70.0	70.0	65.0	70.0	70.0	70.0	70.0	70.0	60.0	70.0	74.8	75.0
La_2O_3	-	-	-	-	-	-	2.5	1.5	-	-	-	-	-	-	1.0
Ta_2O_5	-	-	6.6	2.5	2.5	2.5	2.5	2.5	3.0	4.0	4.0	8.0	4.0	4.0	6.0
CeO_2	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.2	0.2	0.2	0.2	0.2	0.2
GeO_2	-	-	-	-	-	-	-	-	-	-	14.6	-	9.6	-	-
SiO_2	36.9	6.6	-	14.6	14.6	14.6	14.6	14.6	14.6	14.6	-	17.8	5.0	9.8	6.8

GE - SERIES

Oxide	42373-1	51773	51773T	52373-1	6673-1	6773	101673	122073	122673
Li_2O	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
ZnO	6.0	6.0	6.0	8.0	8.0	6.0	10.0	6.0	6.0
Al_2O_3	-	5.0	5.0	2.0	6.0	7.0	5.0	10.0	10.0
B_2O_3	60.0	60.0	60.0	60.0	60.0	60.0	56.0	35.0	31.0
La_2O_3	5.0	-	-	-	-	-	-	-	4.0
Ta_2O_5	8.0	8.0	8.0	7.0	7.0	8.0	8.0	8.0	8.0
CeO_2	0.2	0.2	-	0.3	0.3	0.2	-	-	-
GeO_2	17.8	17.8	17.8	19.7	15.7	-	18.0	38.0	38.0
SiO_2	-	-	-	-	-	15.8	-	-	-
TiO_2	-	-	0.2	-	-	-	-	-	-

V. RADIATION RESISTANCE

The ultraviolet and electron irradiation resistance of the glasses were screened in the facilities described in the following paragraphs.

The ultraviolet exposure chamber was designed to simulate the atmosphere 237 miles from the surface of the earth. Energy from a 20 kW xenon lamp uniformly irradiates a 36 inch diameter area at pressures of 10^{-7} Torr. The length of exposure was 120 hours; 36 samples in a 15 inch square holder were irradiated simultaneously. Figures 7 and 8 show the chamber and sample holder, respectively.

The electron irradiation chamber is a four inch diameter canister, five inches long which utilizes a Sr^{90} source to produce 0.6 MeV beta electrons. The source, purchased in 1967, has a half-life of 28 years and was initially rated at 10 curies. The irradiation area is 2.5 cm^2 which permitted only one glass sample or 2 x 2 cm solar cell to be exposed at one time. Early in the program, the evaluation of resistance to electron irradiation was performed by exposing each glass in the Sr^{90} source for 120 hours. It soon became apparent that this method was consuming too much screening time. To determine the possibility of reducing the exposure time and still obtain significant data, an experiment was conducted with glass No. 22. The same disk was used for a series of exposures as shown in Figure 9 and the results indicated that a 24 hour exposure was sufficient. A similar experiment, using five different samples, was repeated to determine if some of the radiation effects might "bleach" out
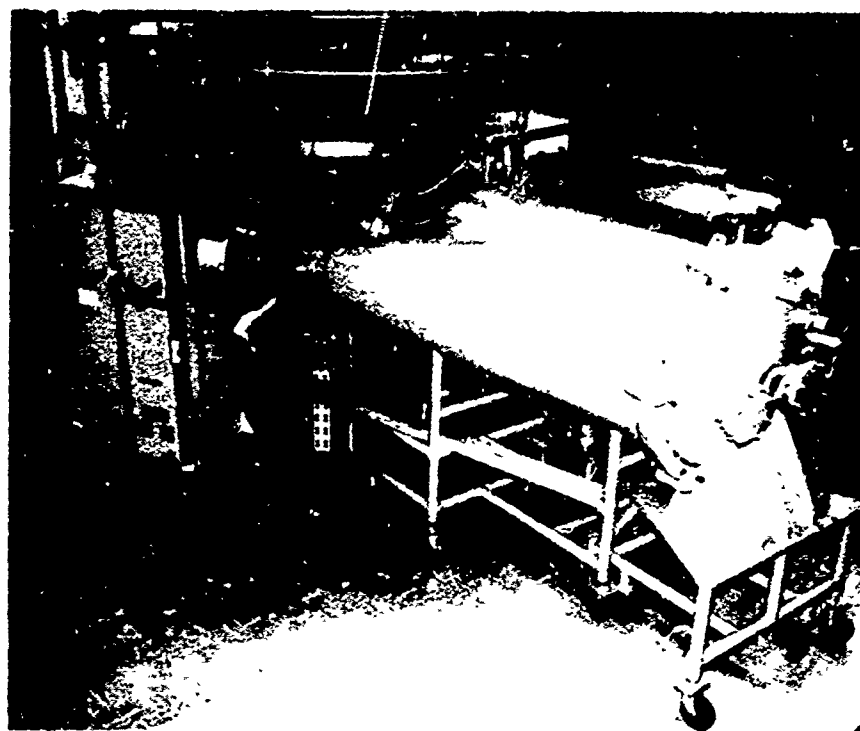
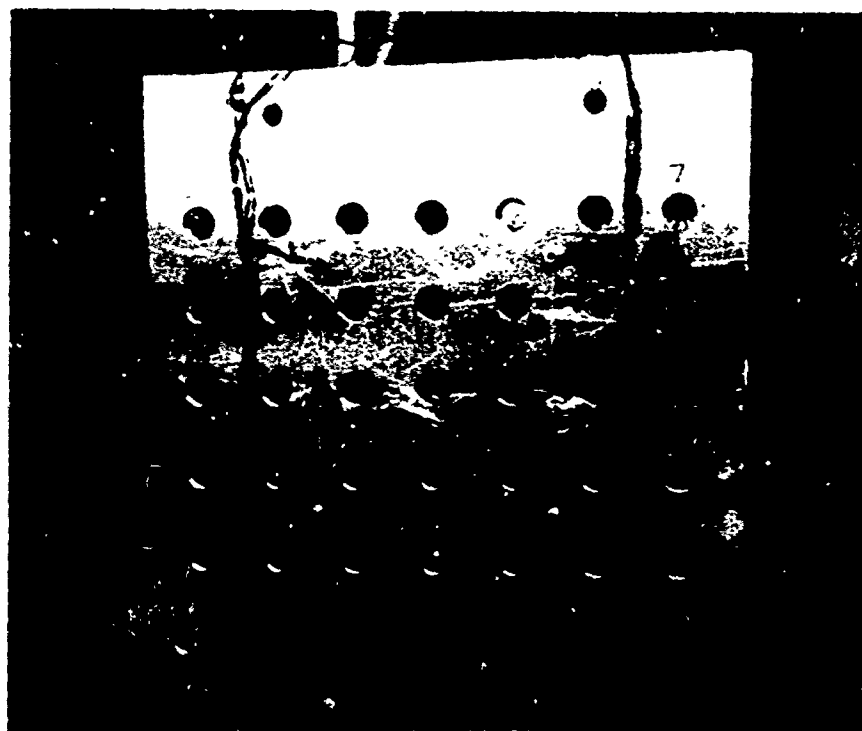Figure 7. Solar simulator used for UV/vacuum exposure.

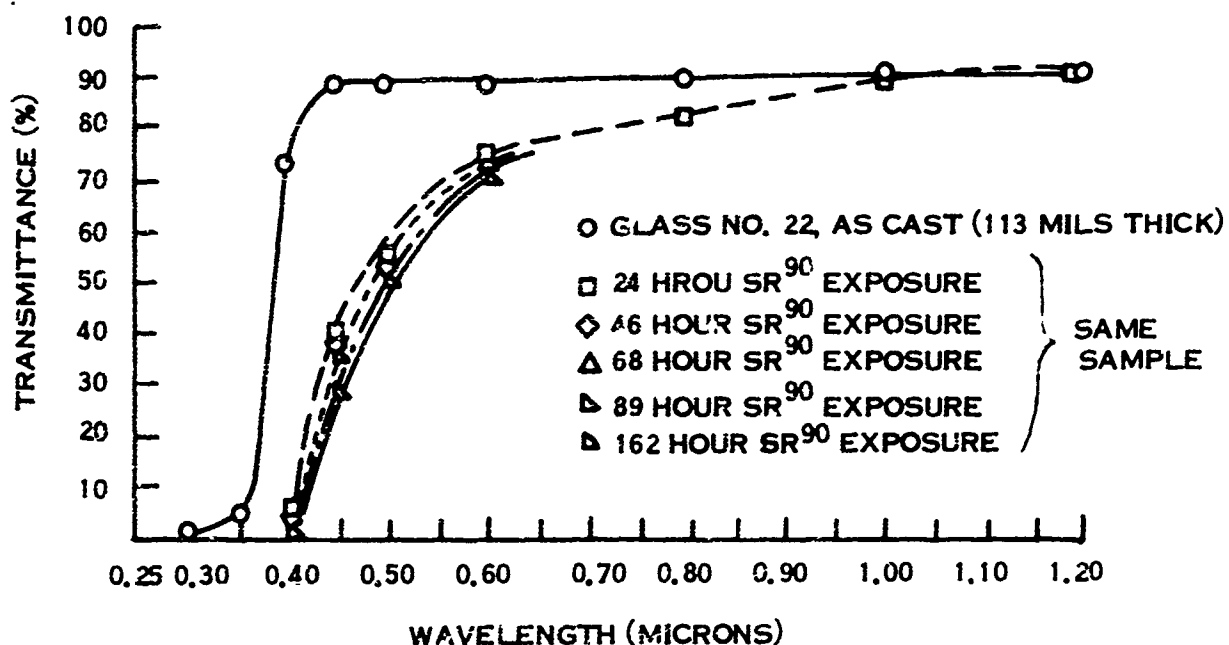Figure 8. Fixture used to hold samples during exposure.

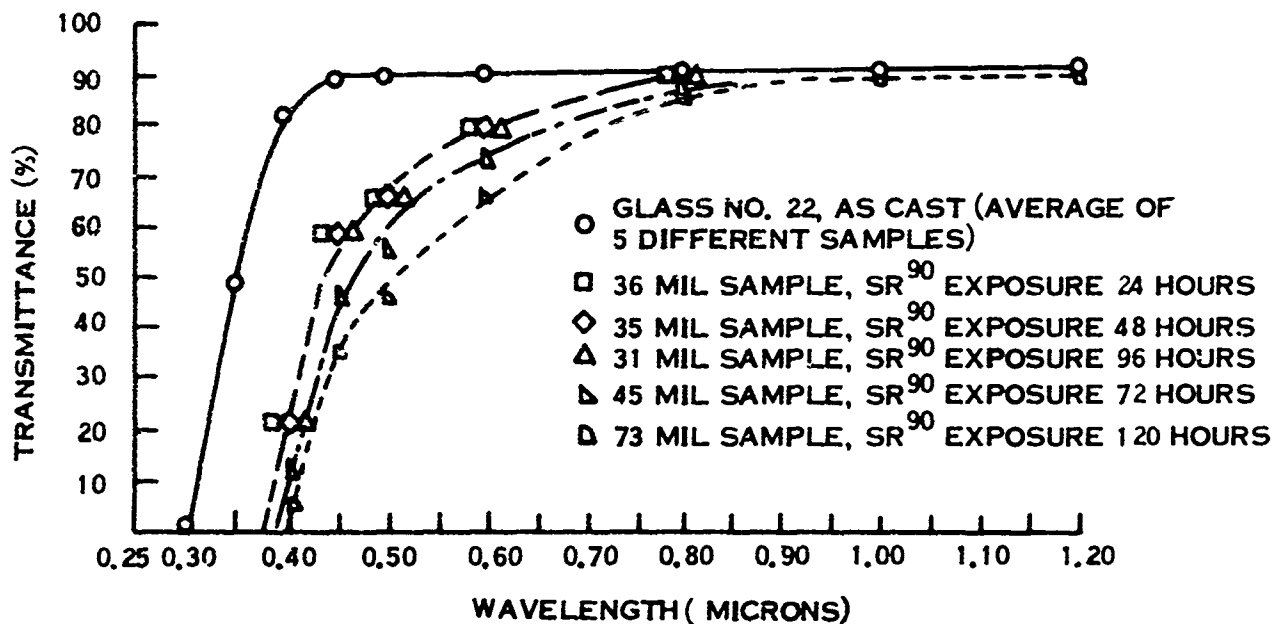Figure 9. Effect of Sr^{90} exposure time on transmission of the same sample of glass No. 22

Figure 10. Effect of Sr^{90} exposure time on transmission of five different samples of glass No. 22

during the time interval the disk was removed from the radiation chamber for transmittance measurements[*]. The results of this work, shown in Figure 10, confirmed a 24 hour exposure time as sufficiently long to produce discerrible radiation effects from which evaluation of different glasses could be made. This latter study also suggests that thicker samples receive more radiation damage. The 31 mil sample, exposed for 96 hours, had a better transmittance (less damage) than the 45 mil sample after only 72 hours of exposure (Figure 10).

The ability of CeO_2 to improve the resistance of glass to radiation damage has been amply described in the literature.[13] This was clearly demonstrated early in our glass development studies. A small amount (0.5 w/o) of CeO_2, added to the parent glass, significantly improved the radiation resistance as shown in Figures 11 and 12. Unfortunately, ceria absorbs in the ultraviolet portion of the spectrum which results in pre-irradiation transmission loss, also shown, in Figure 12.

Late in the program, CeO_2 was replaced with TiO_2 which resulted in some improvement in both pre- and post- irradiation transmission. Figures 13 and 14 show these results.

The effect of composition on radiation resistance was further demonstrated by replacing part of the Li_2O in glass 1TL with Na_2O. The modification, designated 1TLN, had inferior radiation resistance as seen in Figure 15.

---

[*]Normally the post-irradiation transmittance measurements were made within an hour after removing the sample from the Sr^{90} chamber.

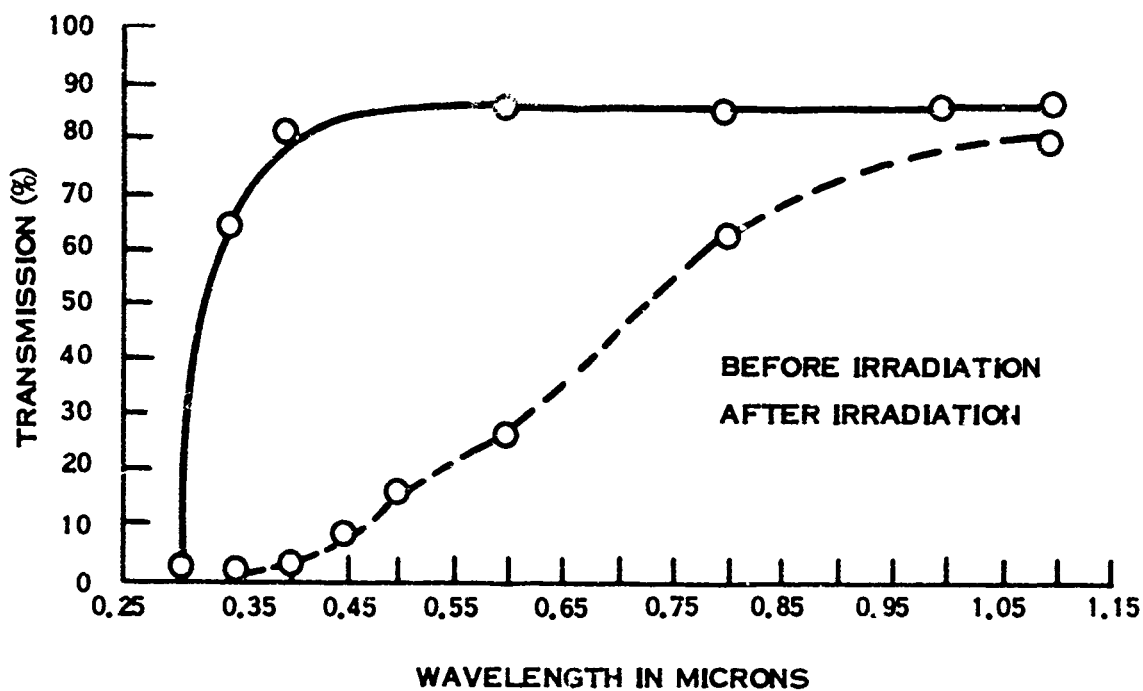Figure 11. Transmission profiles of the parent glass, No. 1, before and after electron irradiation
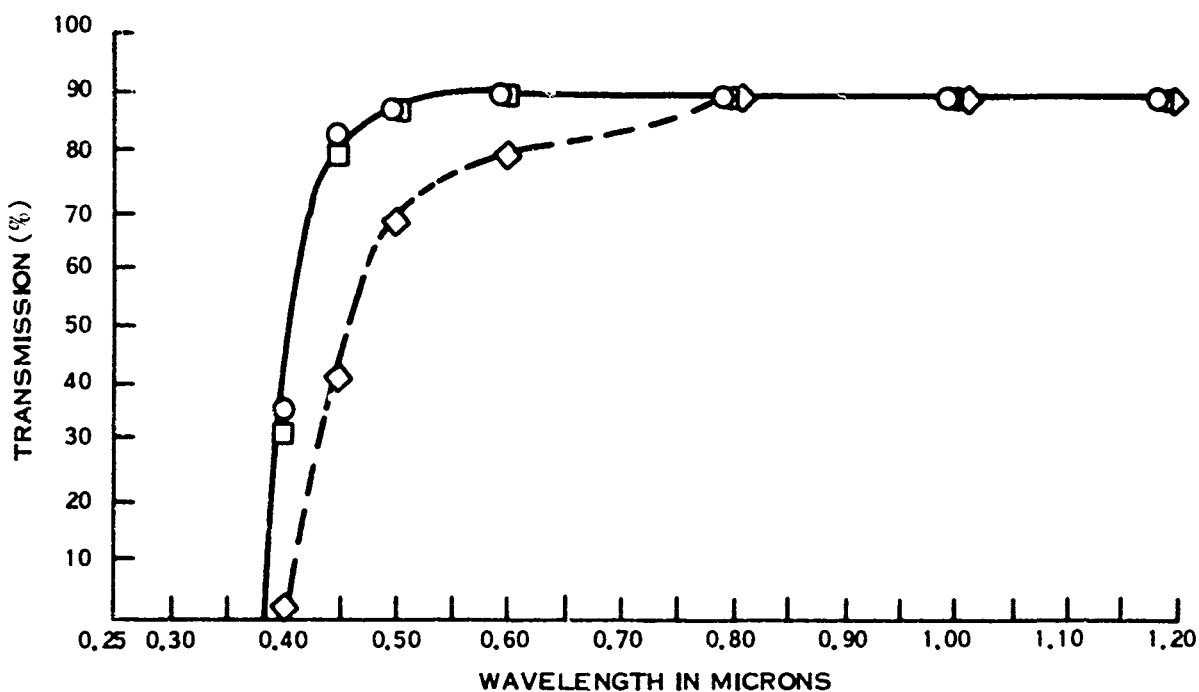

Figure 12. The effect of 0.5 weight percent ceria addition on the radiation resistance of glass No. 1
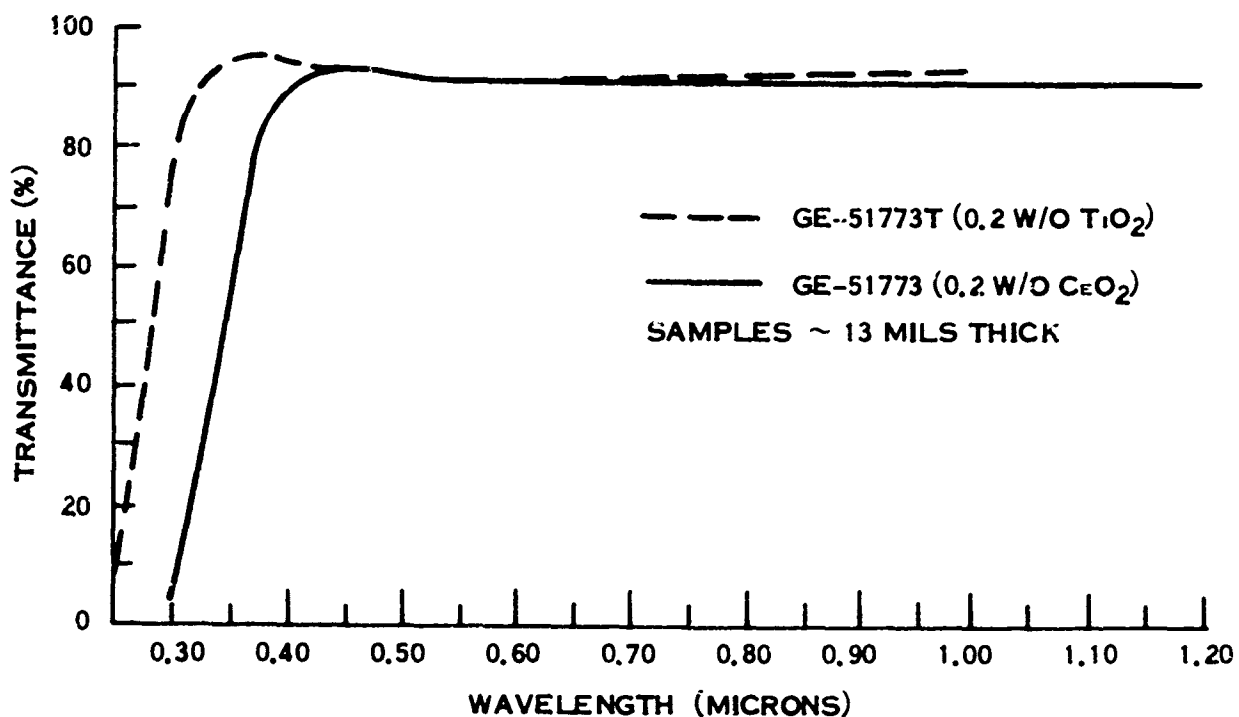
Figure 13. The effect of replacing CeO_2 with TiO_2 on the pre-irradiation transmission of glass GE-51773
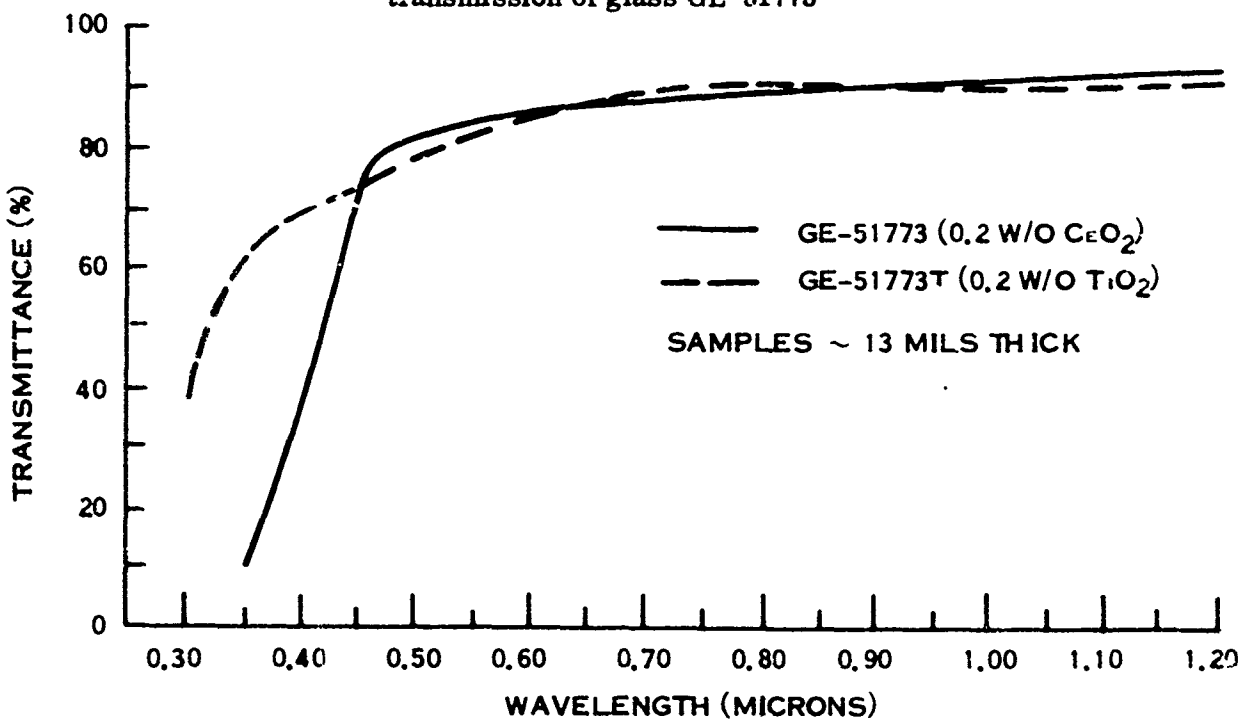

Figure 14. The effect of replacing CeO_2 with TiO_2 on the post-irradiation transmission of glass GE-51773

With the advent of silicon solar cells having a greater spectral response in the shorter wavelengths an effort to further improve the transmission of glasses in this area was made. Both CeO_2 and TiO_2 were eliminated from the glasses with the result that pre-irradiation transmittance increased markedly. Although, post-irradiation data show that radiation damage occurred, some of these glasses transmitted 15% of the incident energy at 0.25 microns after electron irradiation. Figures 16 and 17 are typical transmittance profiles for glasses of this type.

Although glass darkens during irradiation with an accompanying decrease in transmission, especially in the ultraviolet region, the color will fade when the glass is removed from the radiation environment. The length of time required to restore the original transmission is time/temperature dependent, thus "bleaching" can be hastened by heating the irradiated sample. The mechanisms influencing color fading have been discussed by Barber and Richardson[18] and others[19-21] who all agree that composition is a significant factor. We have observed color fading over a period of days at room temperature and in an hour or two at elevated temperatures. In the first instance, two glasses were exposed to Sr^{90} for 24 hours then placed near a window in the laboratory. Within 10 days both samples had regained their original appearance. In the latter instance, another sample of a different glass was exposed to Sr^{90}/24 hours and after its post-irradiation transmission was determined, the sample was heated in air at $100^\circ C$/1 hour, which restored
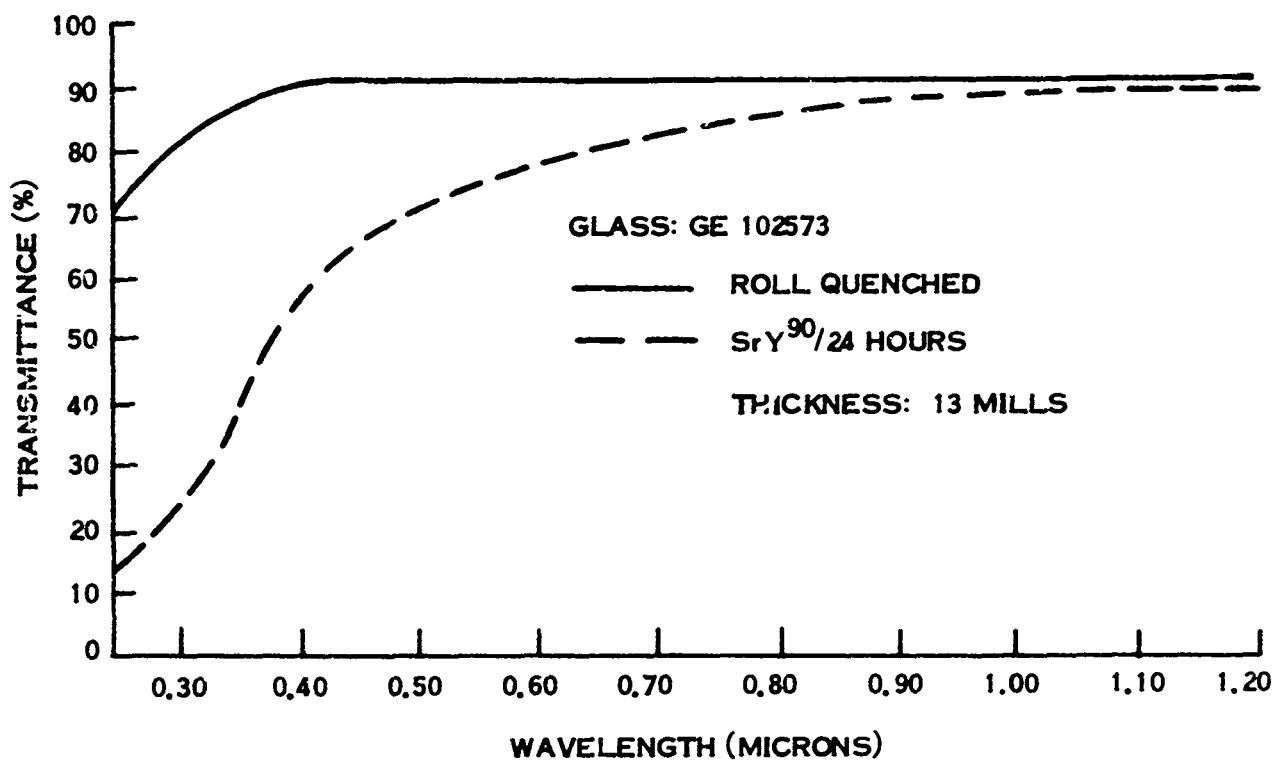
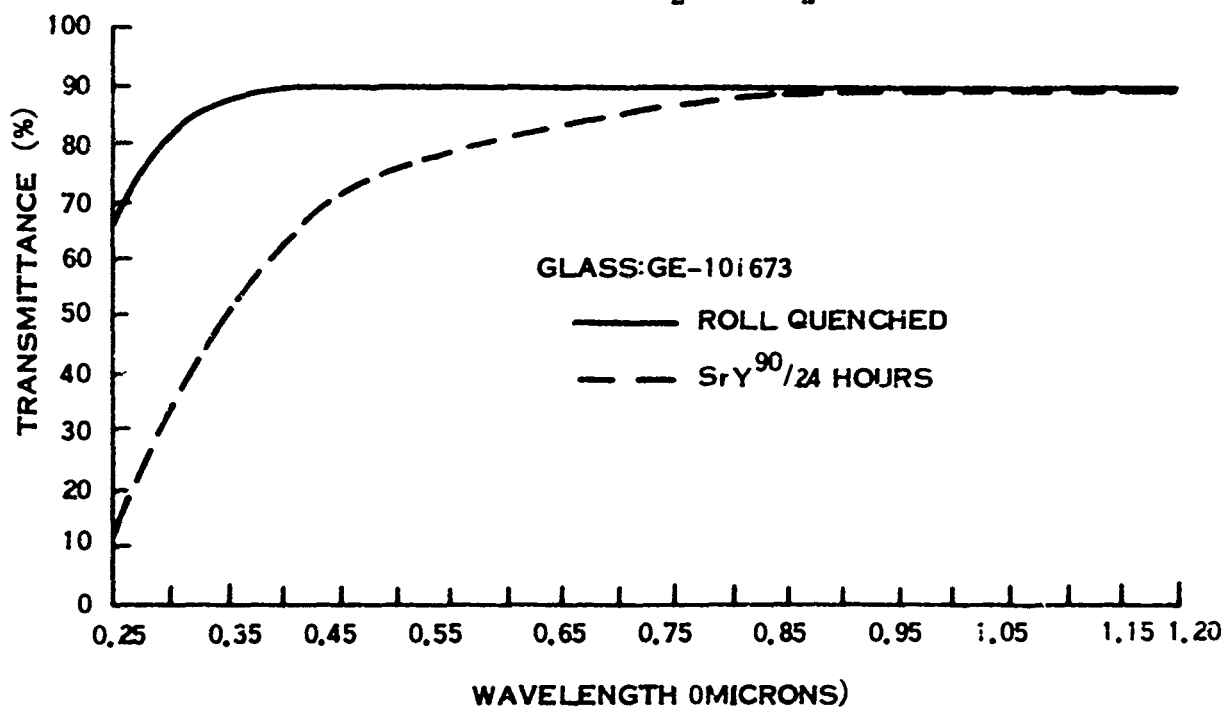Figure 16. Typical pre- and post-irradiation transmission profiles of glasses containing neither CeO_2 nor TiO_2

Figure 17. Typical pre- and post-irradiation transmission profiles of glasses containing neither CeO_2 nor TiO_2

28

the transmission to within 10% of its original value. This data is shown in Figure 18. More recently, a sample of GE-101673 and one of Corning 0211 microsheet were similarly treated, except that the glasses were heated at 80°C in a vacuum of 5 x 10⁻⁶ Torr for one hour. The results of this treatment are shown in Figure 19 A and B.

VI. TRANSMITTANCE CHARACTERISTICS

Transmission profiles were obtained on a Model 99 Perkin-Elmer monochromator coupled to a Gier-Dunkle integrating sphere, which contained a photomultiplier and lead sulfide detectors. The energy source for measurements from 0.25 to 0.35 microns was a Beckman hydrogen lamp. A tungsten strip filament provided the energy for measurements from 0.35 to 1.2 microns. Transmittance measurements at wavelengths shorter than 0.25 microns would require considerably more sophisticated equipment to avoid reflection losses from the fused silica prism in the monochromator.

Measurements routinely were made to 0.35 microns only. However, for those glasses exhibiting any significant transmission at this wavelength, the measurements were extended to 0.25 microns.

Initially the measurements were made on annealed disks about 1" diameter and 80 mils thick. However, after roll queching became established, pieces of glass ribbon about 1" x 1/2" x 14 mils were used.

Most of the more radiation resistant glasses exhibit sharp absorption edges around 0.35 to 0.40 microns and a maximum transmittance of 90% from about
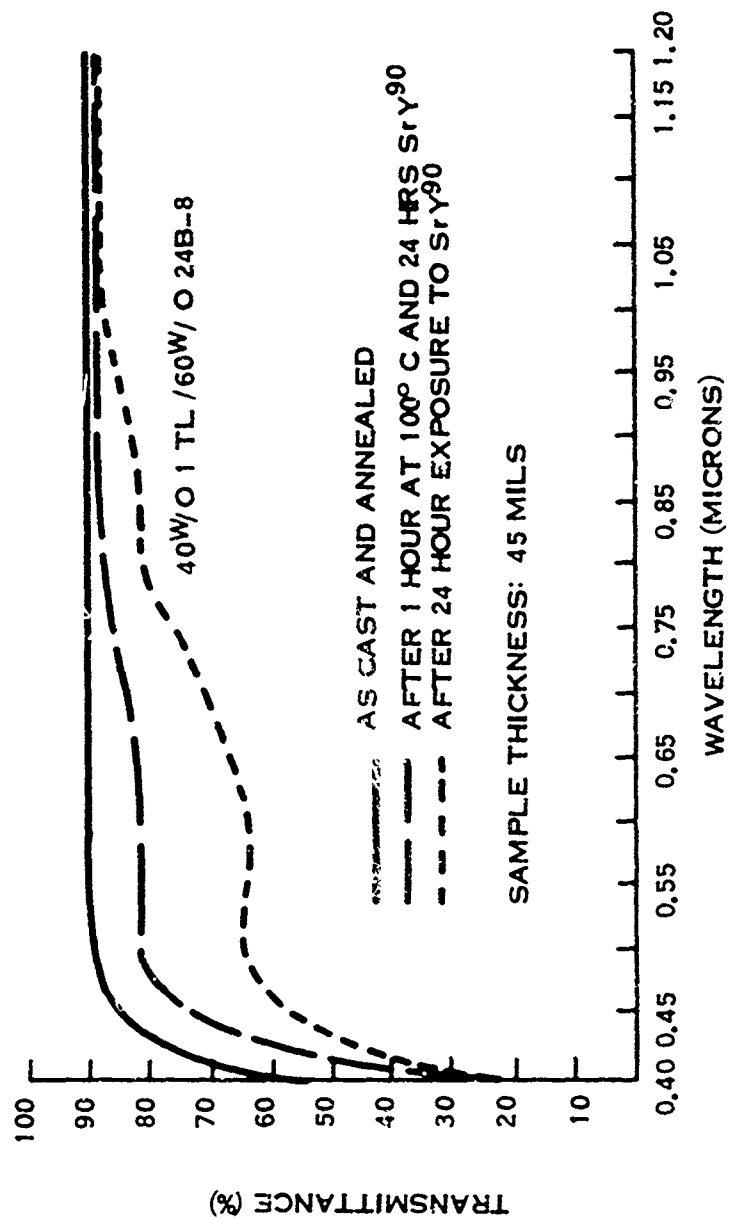
Figure 18. The effect of thermal treatment on color fading of a radiation darkened glass
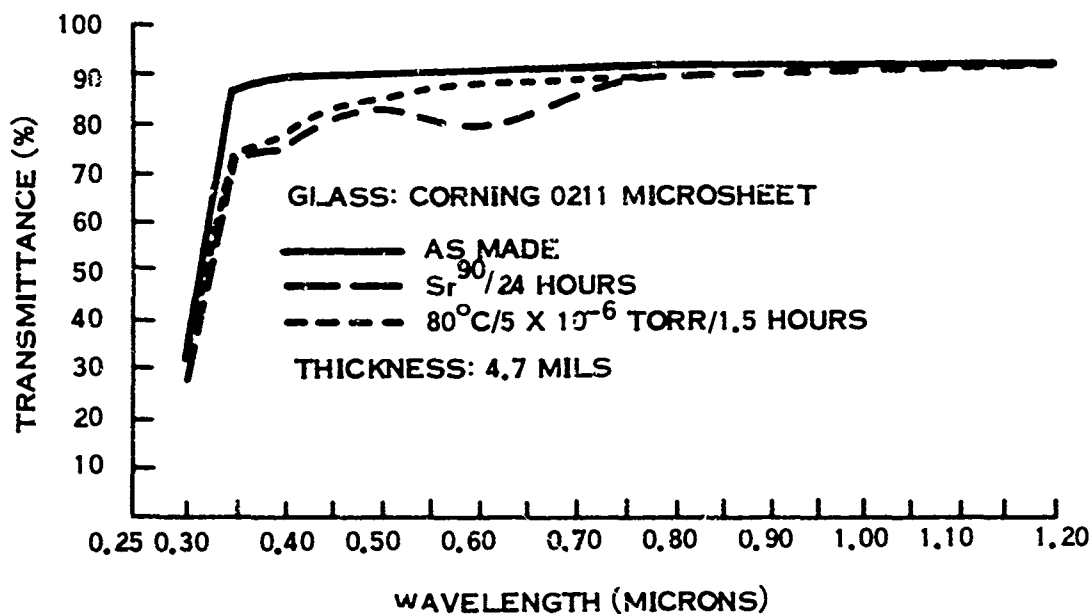
Figure 19A. The effect of thermal/vacuum treatment on color fading of radiation darkened Corning 0211 microsheet
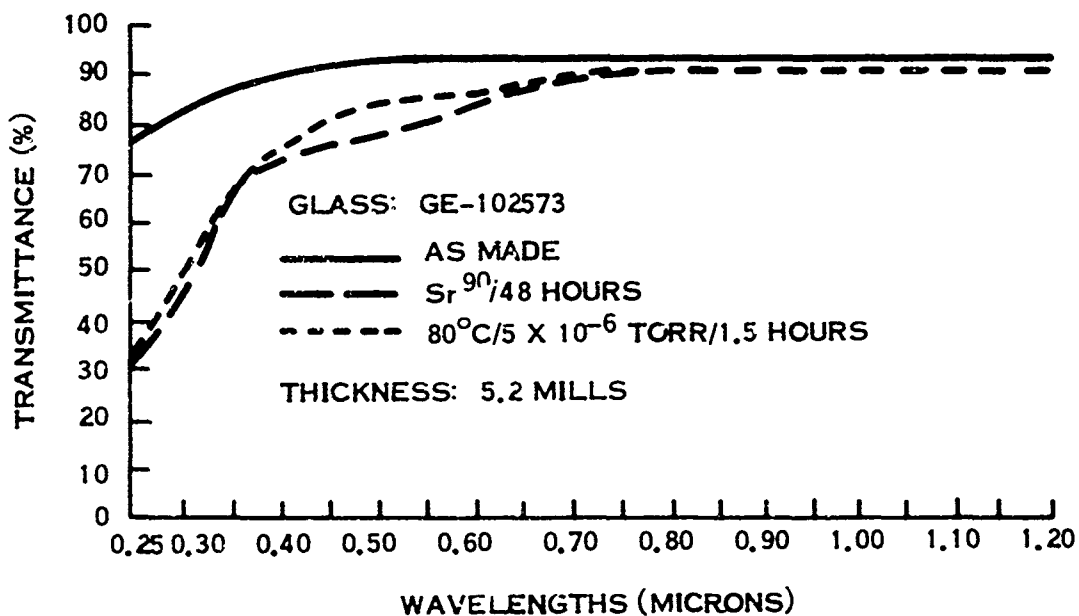

Figure 19B. The effect of thermal/vacuum treatment on color fading of irradiation darkened GE-102573

0.50 to 1.2 microns. Glass 1TL, shown in Figure 5, is typical of this behavior. The addition of Al_2O_3 and Ta_2O_5, increasing the B_2O_3 content, and replacing SiO_2 with GeO_2 increased the maximum transmittance to about 92% from 0.45 to 1.2 microns. Glass HR-12BG, shown in Figure 20, was the first composition to exhibit this behavior.

Some of the lead oxide-containing glasses described in Section IIA exhibited very interesting transmission profiles. In fact, one of these glasses, GE-5973-8, transmitted more energy, before and after irradiation, than any of the other glasses we developed. The peak in the pre-irradiation transmittance data probably reflects some form of luminescence. These data can be seen in Figure 21.

Near the end of the program a series of lead-free glasses was developed which had very high ultraviolet transmission. Some of these glasses had transmittance values over 60% at 0.25 microns and maximum transmittance of 90% from about 0.40 to 1.2 microns. The transmission profiles, before and after irradiation, of two of these glasses are shown in Figures 16 and 17.

It is interesting to note that the high values of transmittance exhibited by many of the glasses developed during this program were obtained from samples which did not have the benefit of an anti-reflection coating. Presumably the application of MgF_2, or a similar material, to these glasses would have resulted in slightly higher values.
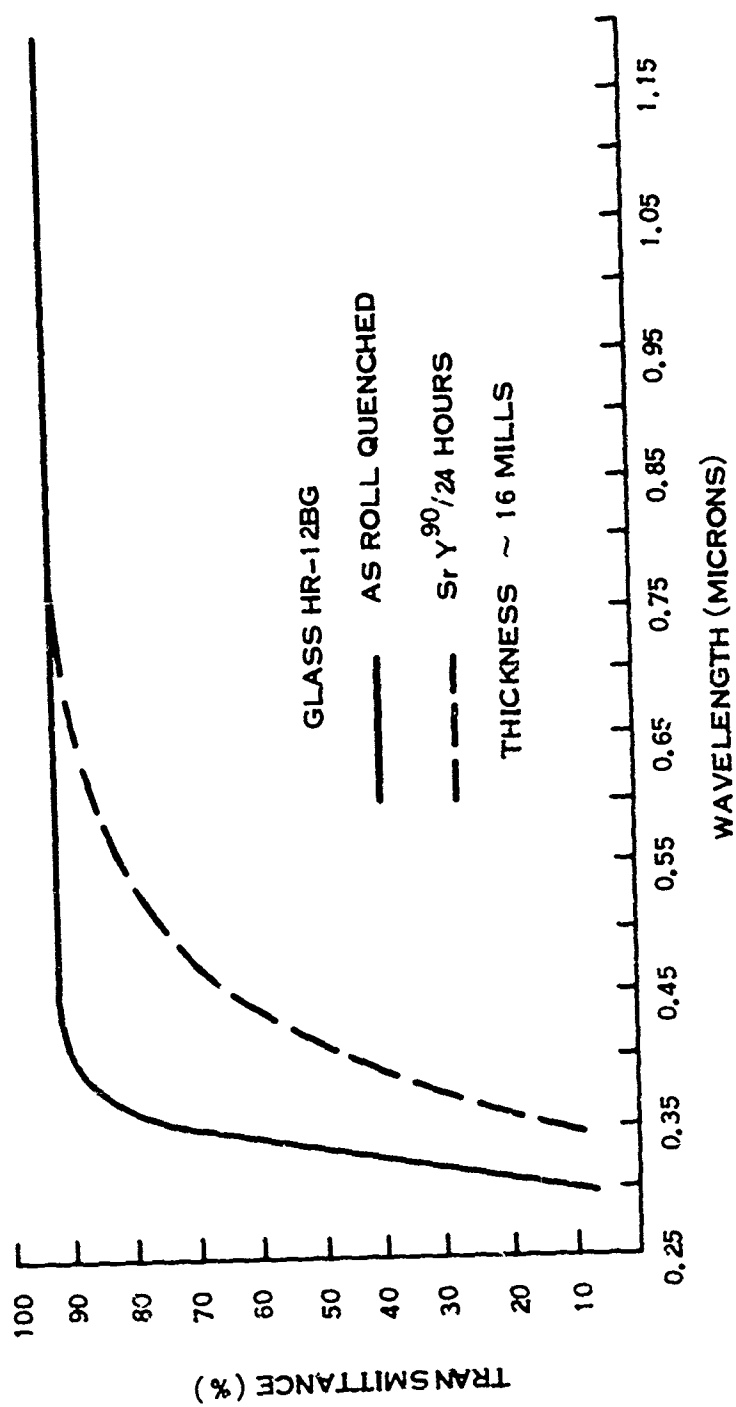
Figure 20. The pre- and post-irradiation transmission of glass, HR-12BG.

GLASS HR-12BG

——— AS ROLL QUENCHED

- - - - Sr Y^{90}/24 HOURS

THICKNESS ~ 16 MILLS

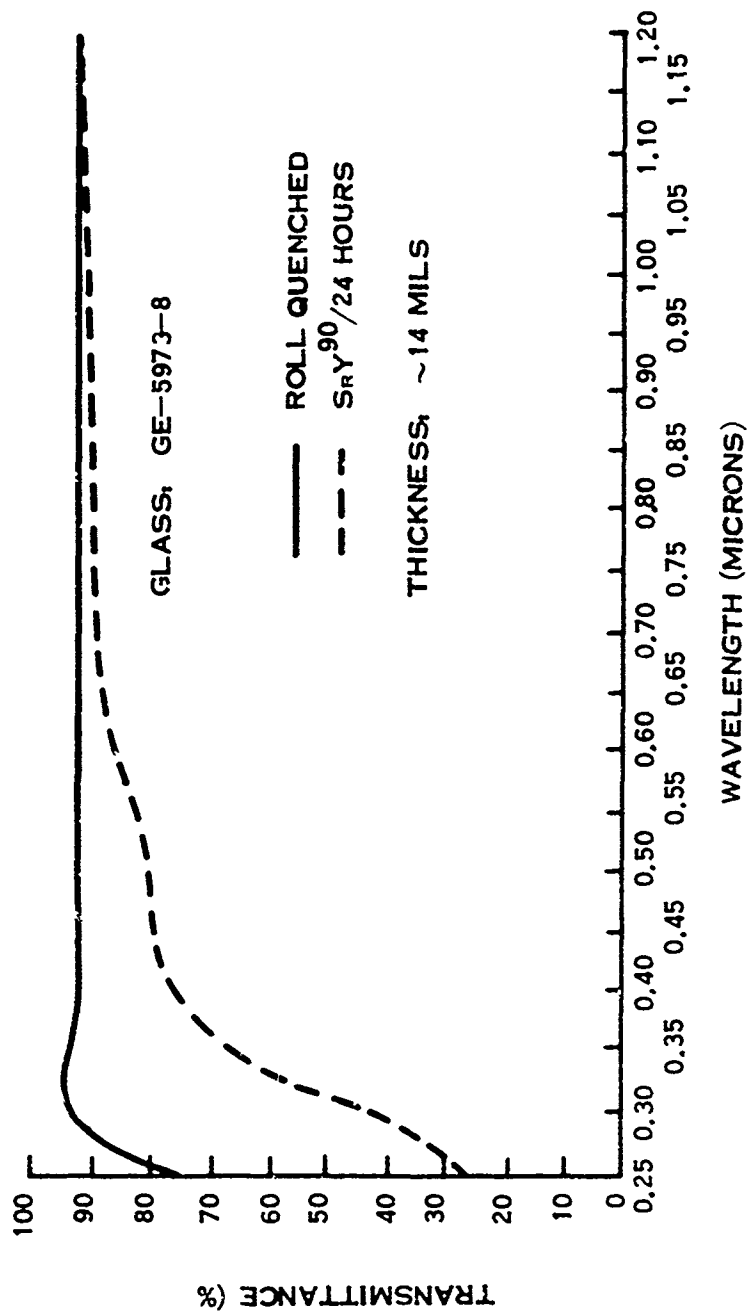WAVELENGTH (MICRONS)

TRANSMITTANCE (%)

33

Figure 21. The pre- and post-irradiation transmission of a lead-oxide containing glass, GE-5973-8.

34

Another interesting observation concerns the effect of substrate on the apparent transmittance of a glass. A wafer of ultrapure fused silica 62 mils thick was coated with 1.6 mils of glass, GE-72673. Pre- and post-irradiation transmittance measurements were made on the uncoated silica, on the coated silica, and on a piece of the GE-72673 glass. The results, shown in Figures 22 and 23, clearly reveal that the optical behavior of the cover glass was upgraded significantly more than the transmission of the fused silica was downgraded.

VII. THERMAL EXPANSION

The linear coefficient of thermal expansion of the glasses was determined with a Brinkmann dilatometer using 1/4 inch square, 2-inch long specimens. This dilatometer contains a resistance heated tubular furnace, fused silica specimen holder, type S (Platinum vs. platinum - 10 percent rhodium) thermocouples, a linear variable differential transformer (LVDT) to sense specimen length changes, and a two-pen, time-base, strip chart recorder. A programmer and electronic controller maintain a constant, preselected rate of temperature increase in the tubular furnace, using the output of a type S thermocouple attached to the furnace wall as a feedback signal. The test specimen rests in a fused silica tube which is attached to the body of the LVDT. The core of the LVDT is attached to one end of a fused silica rod, the opposite end of which contacts the test specimen. Changes in specimen length, then, cause changes in LVDT output which is demodulated and recorded as a function
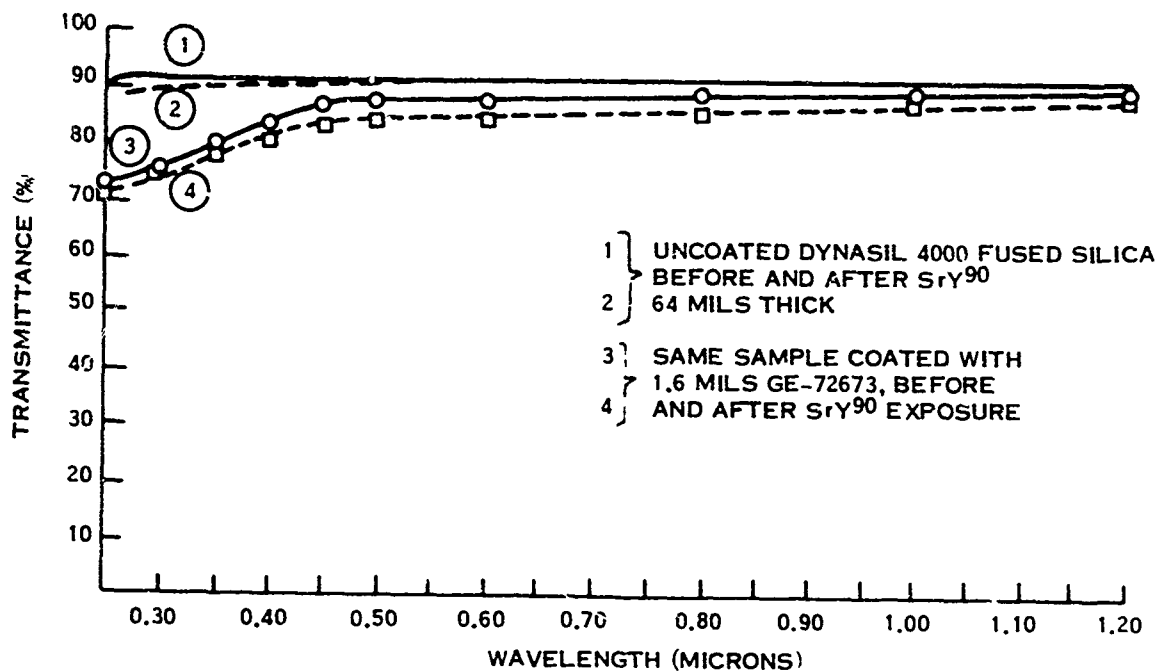
Figure 22. The pre- and post-irradiation transmission of a bare fused silica disk and of the same disk coated with glass, GE-72673
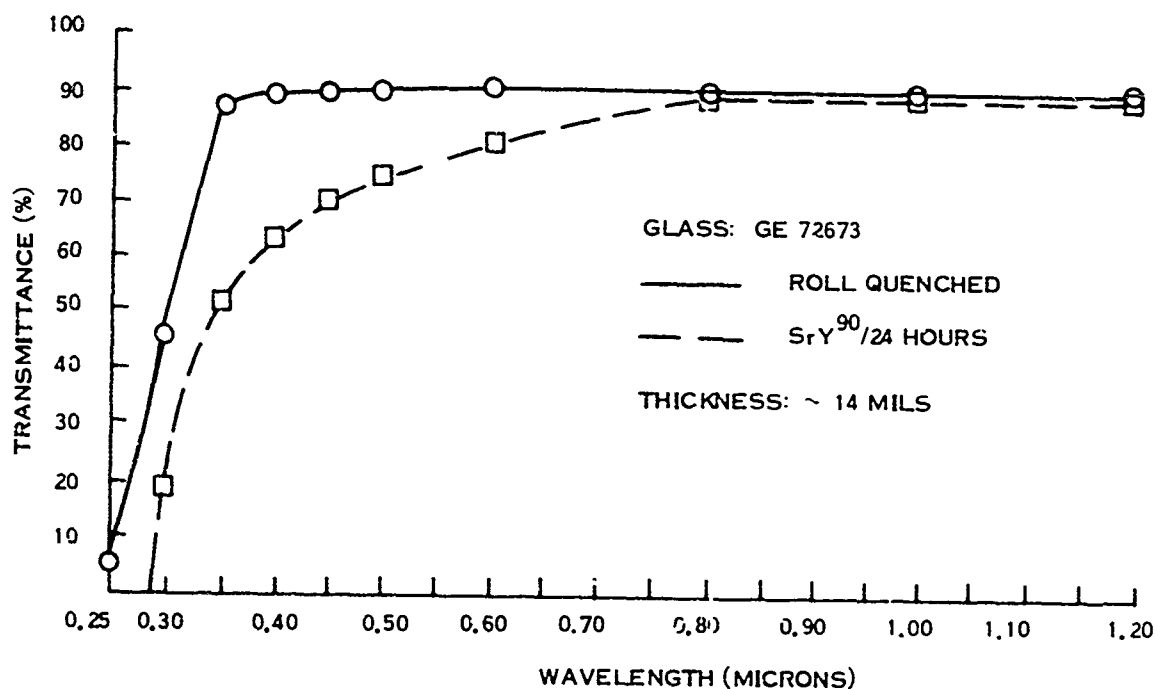

Figure 23. The pre- and post-irradiation transmission of glass, GE-72673

of time on the strip chart recorder. A second type S thermocouple, attached to the test specimen, is used to record specimen temperature as a function of time on the strip chart recorder. A micrometer head is incorporated in the measuring system to directly calibrate the LVDT in place. Thermal expansion of the fused silica measuring system is periodically calibrated using standard specimens obtained from the National Bureau of Standards. The resulting system calibration data are used to correct the raw thermal expansion data for an unknown specimen with a GE M605 computer routine.

The thermal expansion of some initial compositions was as high as 15.9×10^{-6} cm/cm/$^{\circ}$C over the range 25 to 400°C. Compositional adjustments including the addition of Al_2O_3 and Ta_2O_5, decreasing the Li_2O content, and increasing the ZnO content have considerably reduced that value. Recently glasses having expansions of about 6.0×10^{-6} cm/cm/$^{\circ}$C have been routinely developed. While this value is higher than the 4.0×10^{-6} cm/cm/$^{\circ}$C exhibited by silicon solar cells, coatings in excess of 50 microns have been applied.

Figure 24 shows expansion profiles for the parent glass with a coefficient of $9.7 \times 10^{-6}/^{\circ}$C and glass HR-12B4 which has a coefficient of $5.7 \times 10^{-6}/^{\circ}$C. Coefficients of expansion and dilatometer softening point data for other glasses investigated are listed in Table 5.

37
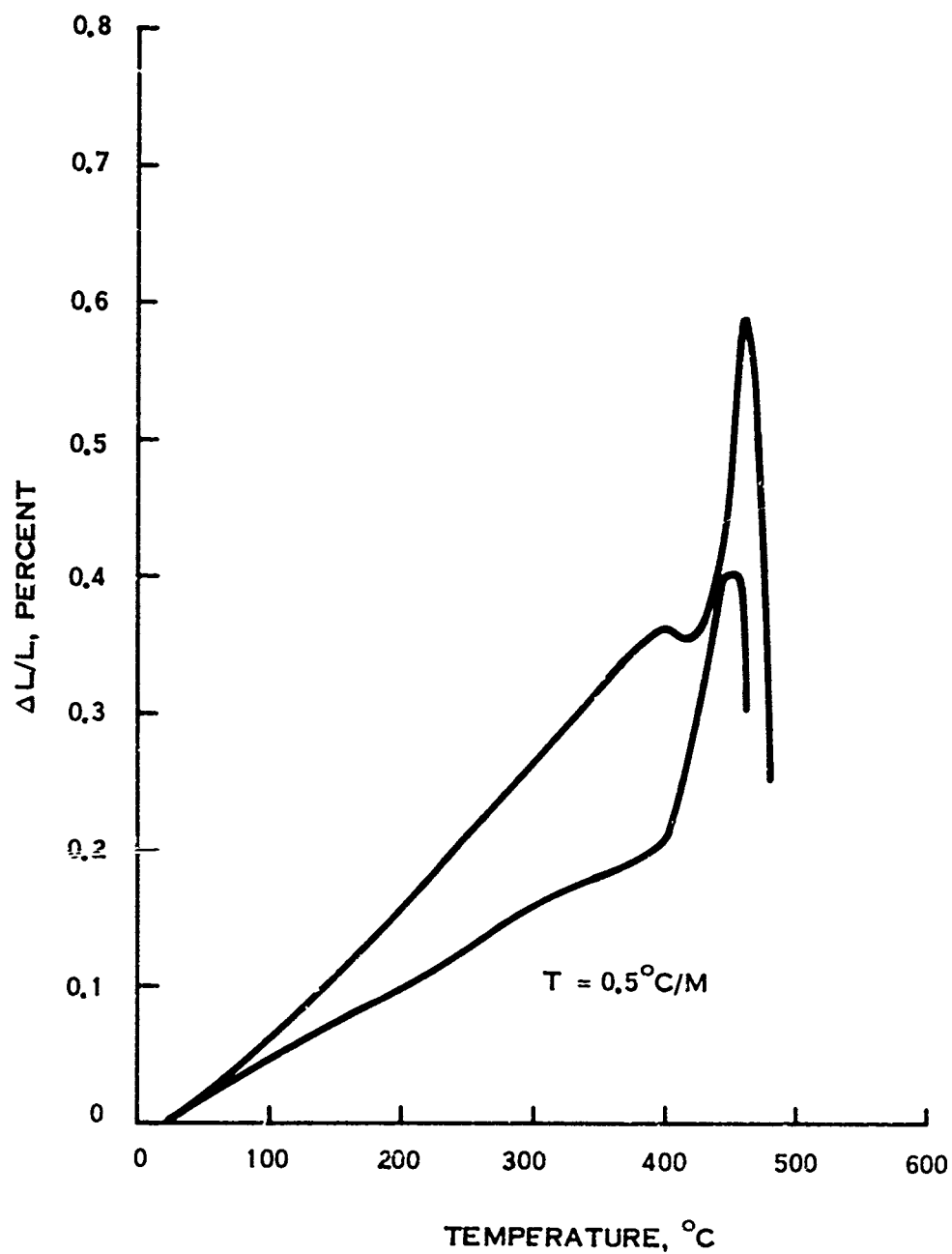
Figure 24. Thermal expansion profiles of the parent glass (No. 1) and of the
lowest expansion glass, HR-12B4

TABLE V. THERMAL EXPANSION COEFFICIENT AND DILATOMETER SOFTENING POINT (DSP) DATA

INITIAL SERIES

Glass No.	Expansion Coefficient*	DSP**
1	9.7	460
1TL	12.2	462
1TLN	13.6	425
24B-8	16.5	395

LEAD GLASS SERIES

HR-16A	8.9	425
HR-16B	8.4	430
GE-2	6.3	470

FINAL SERIES

HR-5	9.5	480
HR-8A	9.9	460
HR-8C	10.1	465
HR-9	6.7	435
HR-9C	6.1	460
HR-9H	6.3	480
HR-10	6.6	470
HR-10A	6.2	470
HR-12B	6.0	460
HR-12BG	6.1	440
HR-12B4	5.7	455
HR-12BG2	6.0	450
GE-6773	6.1	445
GE-42373-1	6.8	460
GE-51773	6.7	480
GE-52373-1	7.2	440
GE-6673-1	6.0	450

* $x\ 10^{-6}$ cm/cm/°C, 25 -400°C

** Corresponds to a viscosity of approximately 10^{12} poises. Not to be confused with softening temperature obtained by ASTM fiber method which corresponds to a viscosity of 4.5×10^7 poises. The latter represents a much more fluid condition.

VIII. SOLAR CELL COATING AND CHARACTERIZATION

A. Coating Technique

The application technique we have used is principally one involving sedimentation of very fine glass particles from an ethyl acetate/isopropyl alcohol slurry onto a silicon solar cell. Glass ribbon, ball milled to pass through a 200 mesh sieve, is mixed with the ethyl acetate/isopropyl alcohol and the slurry is poured onto a solar cell positioned in a shallow container. After a brief time period to allow a sedimented layer to form, the excess slurry is siphoned off for re-use. The slurry-coated cell is then dried and subsequently heated at a temperature which fuses the particles to each other and to the solar cell. Modules consisting of nine solar cells, in a 3 x 3 cell symmetry, have also been coated by this method. The cell interconnects also to receive a glass coating by this technique.

Although we have successfully coated many individual silicon solar cells and several 9-cell modules by the fusion method, we believe that these glasses could also be applied by most of the other integral cover techniques being investigated, if desirable to do so.

B. Characterization

Initially, N/P aluminum contacted and P/N lithium-doped aluminum contacted cells were studied in the program. I-V response data revealed that the P/N lithium doped cells were very temperature-sensitive; a fusion cycle of 510°C/30 minutes degraded their electrical performance below an acceptable

level. Subsequent data supplied by AFAPL confirmed that a cycle of $500^\circ C$ 10 minutes was a maximum temperature-time profile.

The N/P aluminum-contacted cells were only slightly less temperature-sensitive. Integrally covering these cells in a fusion cycle of $520^\circ C/18$ minutes produced marginally acceptable I-V responses.

In Figure 25 the I-V responses of bare and integrally covered P/N and N/P aluminum contacted cells are shown. Coating the P/N lithium doped cells caused considerable reduction in curve factor at temperatures as low as $510^\circ C$.

The best experimental results obtained to date on aluminum contacted N/P cells have been with glass composition HR-13C and HR-13D fired at a temperature time cycle of $520^\circ C/18$ minutes. Cells containing HR-13C which had been applied at $520^\circ C/18$ minutes, had efficiencies in the vicinity of 8.3 to 8.7 percent with maximum power approximating 47 milliwatts. Cells coated with HR-13D had efficiencies in the vicinity of 8%.

Effort was also directed toward cover glass development for N/P silver-titanium contacted cells. While the temperature constraints are not as severe for these cells, they definitely exist as Figure 26 clearly demonstrates. The two glasses (HR-12BG and HR-12B) used to cover the cells are almost identical in terms of composition and transmission characteristics. Initial efficiencies of the cells were slightly better than 10%. Essentially no degradation occurred during a fusion cycle of $575^\circ C/4$ minutes, the efficiency being 9.9%. However, after 8 and 15 minutes at $575^\circ C$ the efficiency decreased to 8.3 and 6 percent,

41
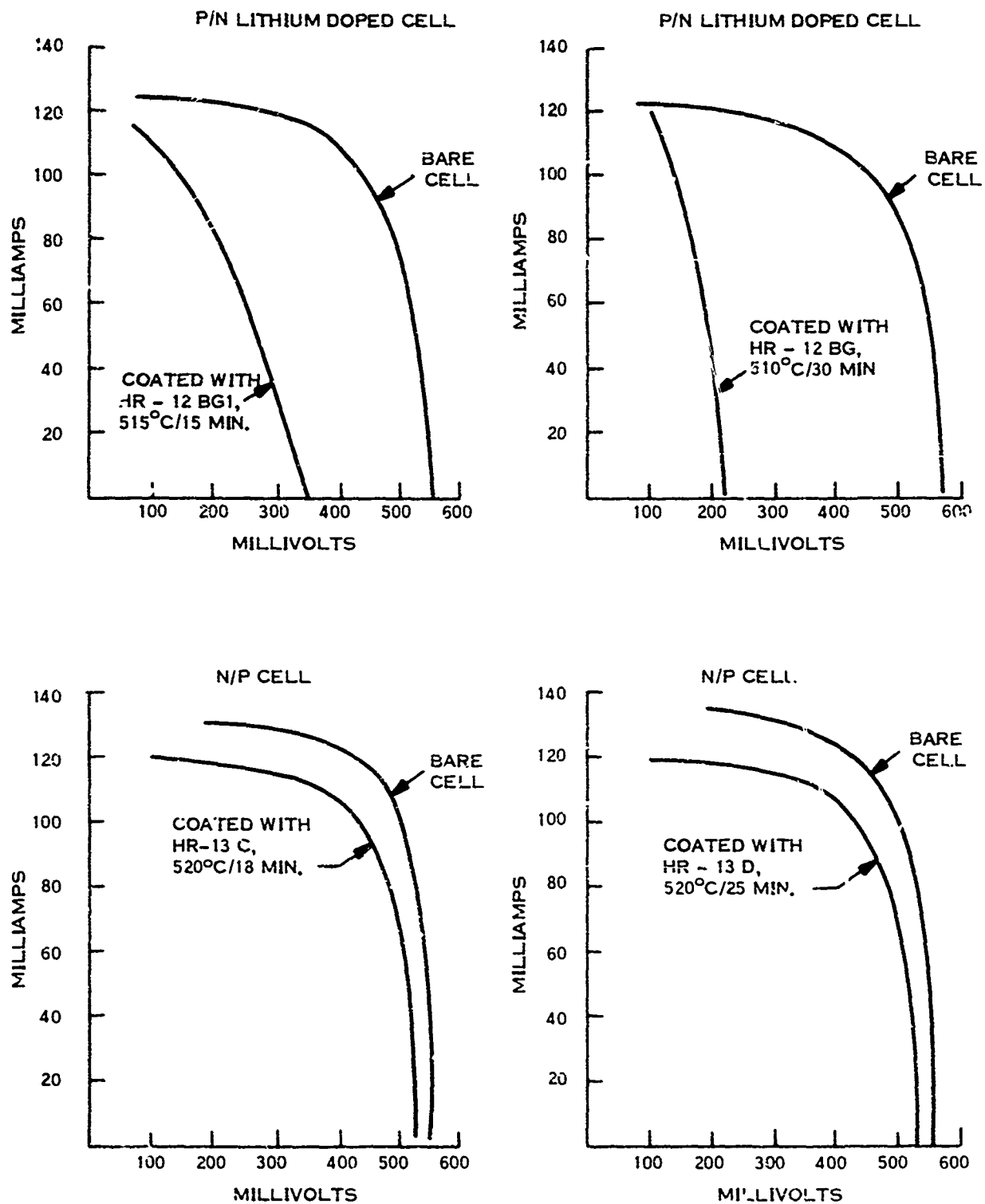
Figure 25. The Effect of Fusion Cycle on the I-V Response of Integrally
Covered Aluminum-Contacted Silicon Solar Cells

SYMBOL	FIRING TIME	GLASS	THICKNESS	P_{MAX}	EFFICIENCY
———	4 MIN.	HR-12BG	2.5 MILS	55.6 MW	9.9%
— — —	8 MIN.	HR-12B	1.5 MILS	46.4 MW	8.3%
—·—	15 MIN.	HR-12B	2.0 MILS	33.6 MW	6.0%

INITIAL EFFICIENCY – 10.0%
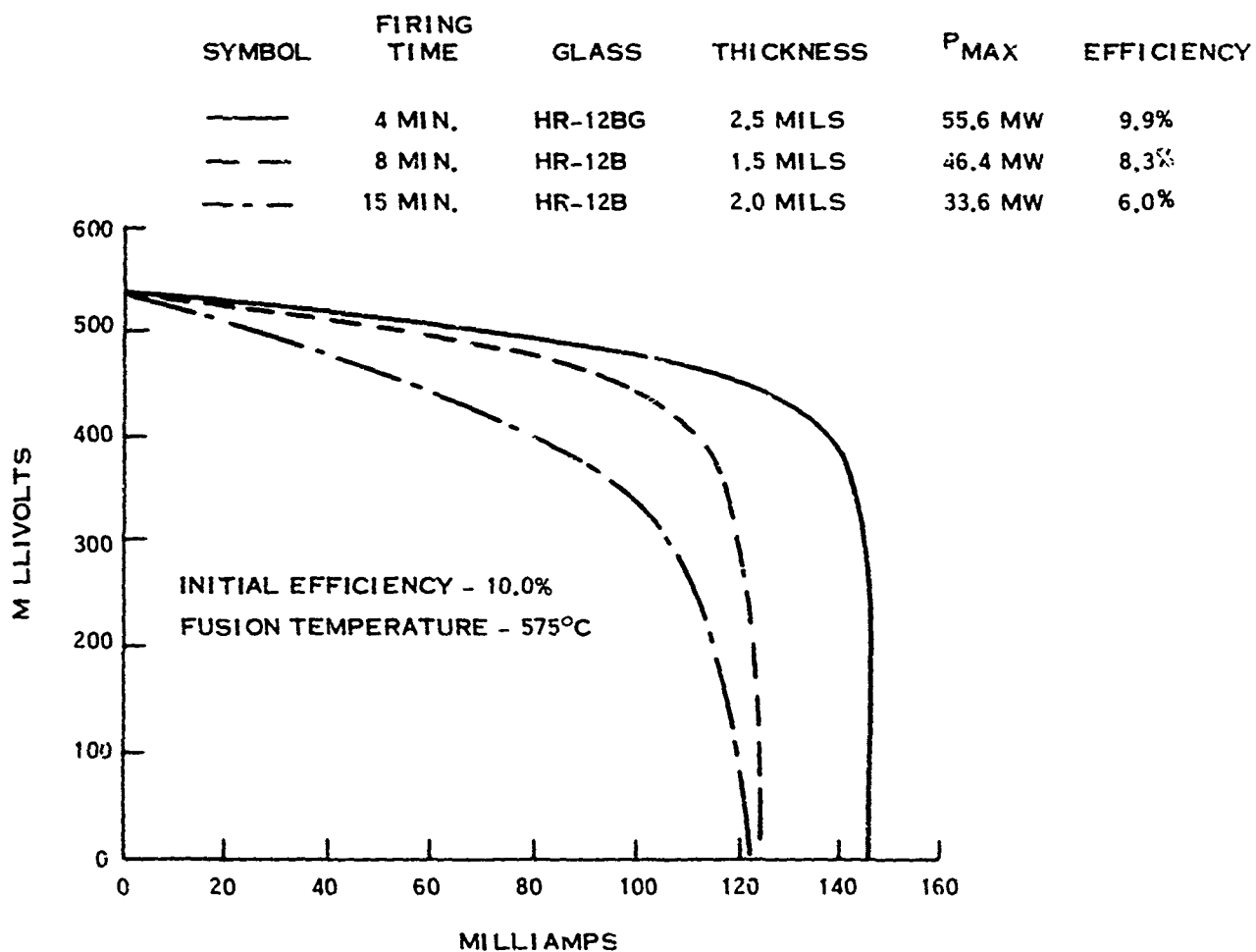
FUSION TEMPERATURE – 575°C

Figure 26. The effect of various fusion times (same temperature) on the I-V response of integrally covered N/P silver/titanium-contacted silicon solar cells

respectively. Lower temperatures and longer time cycles decreased efficiencies. For example, application of HR-12BG at 540°C/25 minutes decreased the efficiency to 8.1%.

The effect of humidity on integral glass covers applied to N/P silver/titanium-contacted silicon solar cells was investigated. I—V response data were obtained on the bare cells, on the cells after integral covering, and on the covered cells after exposure to 90% R.H./38°C for 30 days. Twenty cells were subjected to these conditions.

Typical data obtained from one of the four sets of five cells are shown in Figure 27. The apparent contradictory behavior exhibited by these data may be related more to establishing good electrical contact during I-V measurements than to cell damage during glassing.
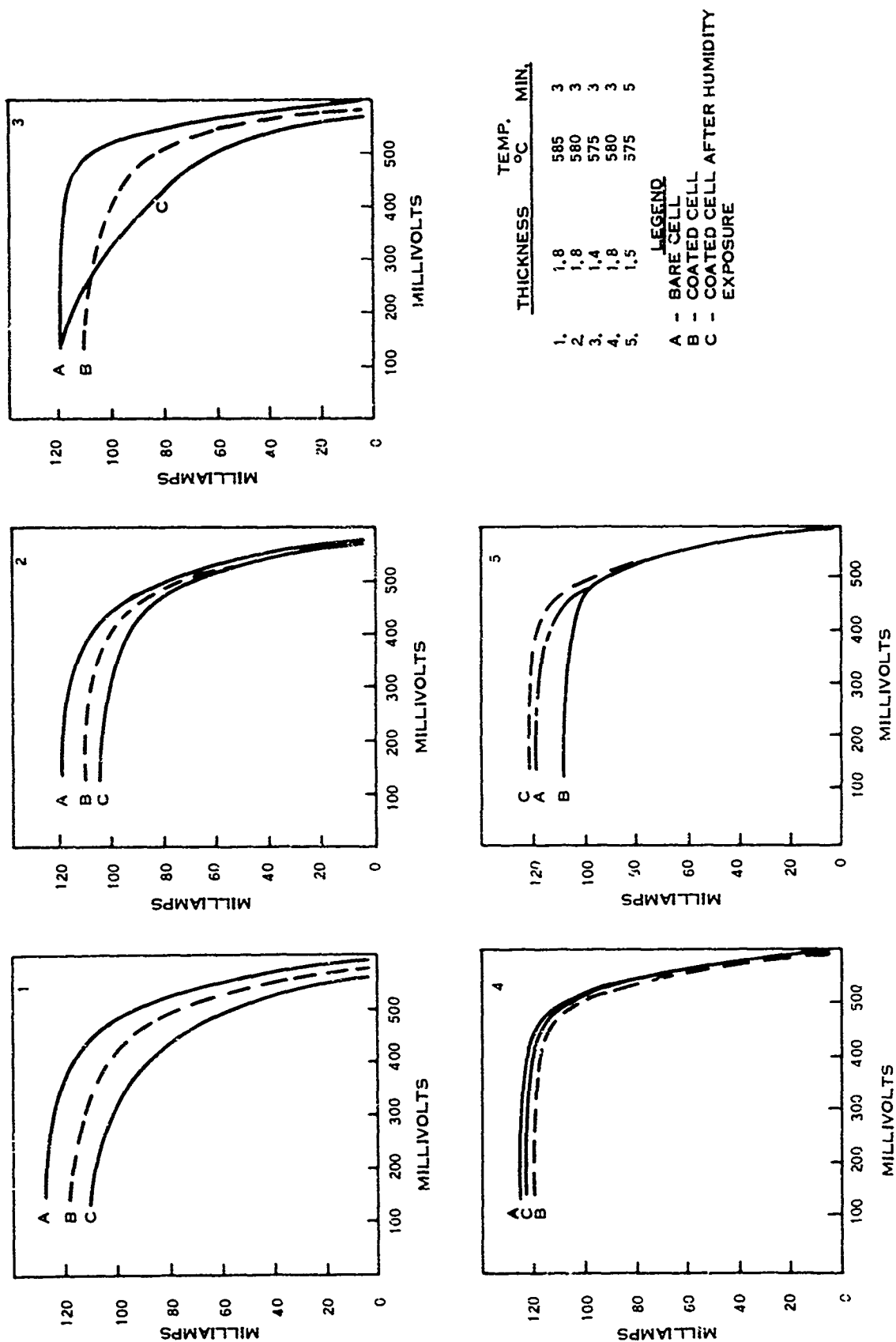
Figure 27. The Effect of 30 Day Humidity Exposure on the I-V Response of N/P Silver/Titanium–Contacted Cells Integrally Covered With Glass, HR–12BG

C. Solar Cell Module Fabrication

The initial planning for this program, over four years ago, included the demonstration of the coating process on nine cell modules of various types of solar cells and interconnections. When the time came to order these modules (Spring 1973), lack of sufficient demand, changes in the industry, and general shortages, etc., all led to the unavailability of production modules. Special arrangements were then made, with considerable difficulty, to have the vendors set up to prepare a few modules for use in completing this phase of the program. This took over a year with more than half of the time extending beyond the completion of other aspects of the program. All parties concerned performed valiantly in attempting to provide the desired modules within the limited budgets of time and funding. Unfortunately, the results were not as good as one would expect if the cells, modules, and coatings were being more continuously produced. Nevertheless, the coatings and process still appear to have a great deal of promise for providing low cost solar cell protection.

Ten modules of nine cells each were prepared through the combined efforts of the Systems Group of TRW, Inc. and Centralab Semiconductor. These were as follows:

1. Modules 1-4 (in Table VI) were parallel gap welded with Invar silver interconnections and delivered by TRW, Inc. using nine N/P cells, for each module, with silver/titanium contacts prepared by Centralab.

2. Module 5 was fabricated by TRW using ultrasonically welded aluminum interconnections on N/P aluminum contacted solar cells (10 ohm-cm, polished).

3. Modules 6-10 were fabricated by Centralab using N/P aluminum contacted cells and ultrasonic welding of the aluminum interconnects.

Pre-glassing current-voltage characterization of the N/P silver/titanium contacted solar cell modules 2 through 4 showed open-circuit voltage of 1.34 to 1.44 volts and short-circuit currents of 360 to 370 milliamperes. Module 5, containing N/P aluminum contacted cells had a V_{oc} of 1.5 volts and an I_{sc} of 350 milliamperes. Because of two cracked cells, module 1 gave I_{sc} of 235 milliamperes along with V_{oc} of 1.45 volts.

Modules 6-10, as received, showed short-circuit currents of 100 to 120 milliamperes and open-circuit voltages of approximately 1.4 volts. The poor curve factor of these cells was attributed to overheating during welding.

As detailed in Table VI, the surface quality of the cells affected the glassivation process. As a result, post-characterization measurements were not made on the Centralab modules.

The pre- and post-glassivation current-voltage curves are shown in Figure 28 for modules 2, 3 and 4. They showed an approximate 15 to 20%

decrease in short-circuit current. However, there was little change in open-circuit voltage, which is the parameter most sensitive to the glassing process. Module 3 tended to have a higher curve factor than modules 2 and 4.

Single cells procured earlier from Centralab were coated and fired with the modules. The N/P silver/titanium cells which were fired with modules 1, 2, 3 and 4 had efficiencies of 9.8 to 9.9% with curve factors similar to the one in Figure 26 after a firing cycle of 4 minutes at 575°C. As a result, conclusions as to the compatability of various cell and contact metallization types with the selected glasses can best be based on the aforementioned results with the single cells.

TABLE VI

SUMMARY OF MODULE CHARACTERISTICS AND CONDITIONS

| Module No.	Solar Cell Contacts	Solar Cell Vendor	Module Characteristics	Module Fabricator	Glass Cover	Fusion Cycle	Comments
1	Ag/Ti	Centralab	Invar (25 μm) silver plated interconnectors, parallel gap welded.	TRW	HR12-BG	565°C/ 5 min.	Inferior quality cell surface (streaks, unremovable stains, blotches, discoloration, imbedded surface particles). Adversely affected glassivation process. Rugged module construction. Withstand fusion cycle. Pre- and post-glassivation I-V characteristics measured. Two cells damaged during pre-glassing characterization.
2	Ag/Ti	Centralab	Same	TRW	HR12-BG	580°C/ 5 min.	Inferior quality cell surface (streaks, unremovable stains, blotches, discoloration, bonded surface dirt). Adversely affected glassivation process (poor adhesion over blotched zones, multiple surface streaks and blemishes hindered wetting and caused pinholes). Excellent module construction and cell interconnection. Withstood fusion cycle. Pre- and post-glassivation characteristics measured.
3	Ag/Ti	Centralab	Same	TRW	HR12-BG	570°C/ 6 min.	Inferior quality cell surfaces. Glassivation affected by surface condition in selected areas (aggregation and spalling over blotched areas, rough surface over imbedded particles, poor surface wetting in streaked zones). Excellent module construction. Withstood fusion cycle. Pre- and post-glassivation I-V characteristics measured.
4	Ag/Ti	Centralab	Same	TRW	HR12-BG	570°C/ 5 min.	Inferior quality cell surface affected glass wetting and adhesion. Module construction withstood fusion cycle. Pre- and post-glassivation I-V characteristics measured.
5	Al	Centralab	Aluminum interconnects (38 μm); ultrasonically bonded.	TRW	HR-13C	520°C/ 4 min.	Inferior quality cell surface (streaks, unremovable stains, imbedded dirt, discoloration, rough areas). Adversely affected glassivation process. Glass covered evenly in defect-free areas. Agglomerated and streaked in other areas with resultant roughened surfaces. Cell metallization did not withstand fusion cycle, resulting in lifting of interconnects. Pre-glassivation I-V characteristics measured only.
6-10	Al	Centralab	Ultrasonic weld of one Al input lead and output lead.	Centralab	HR-13C	520°C/ 4-18 min.	Several interconnection tabs missing on modules as delivered. Input-output leads disconnected in some cases. Pre-glassivation I-V measurements showed V_{oc} of ≈ 1.4 volts and I_{sc} of 100 to 120 ma. Inferior cell surface quality adversely affected glassivation process. Module construction did not withstand fusion cycle. Post-characterization measurements not made.
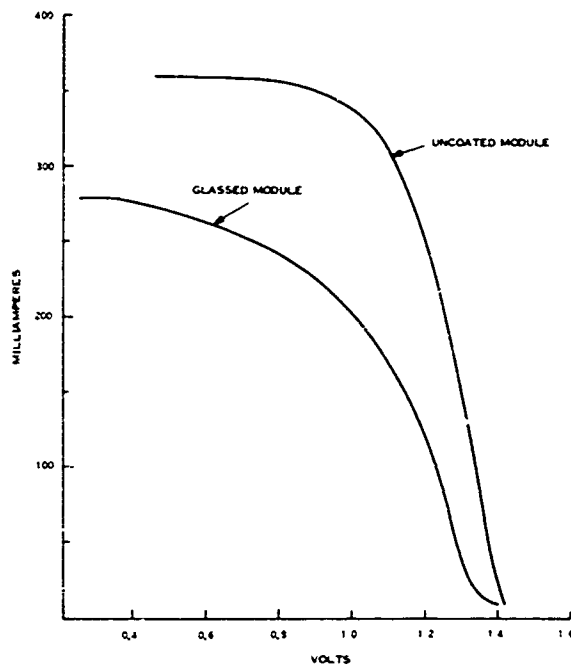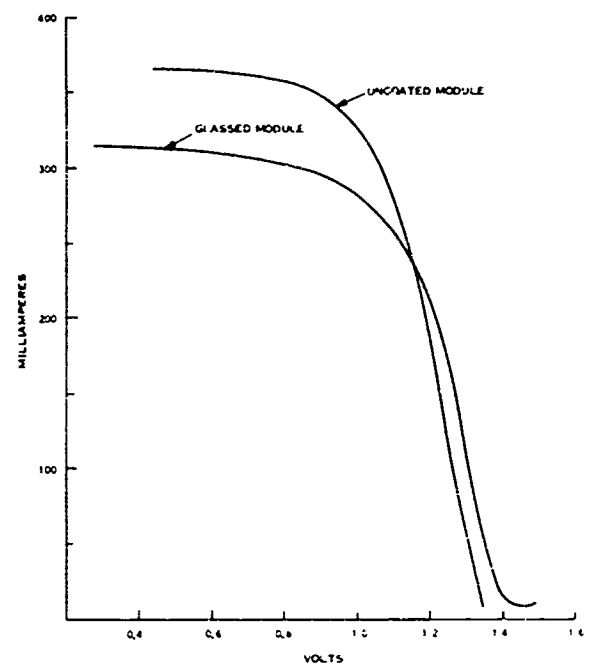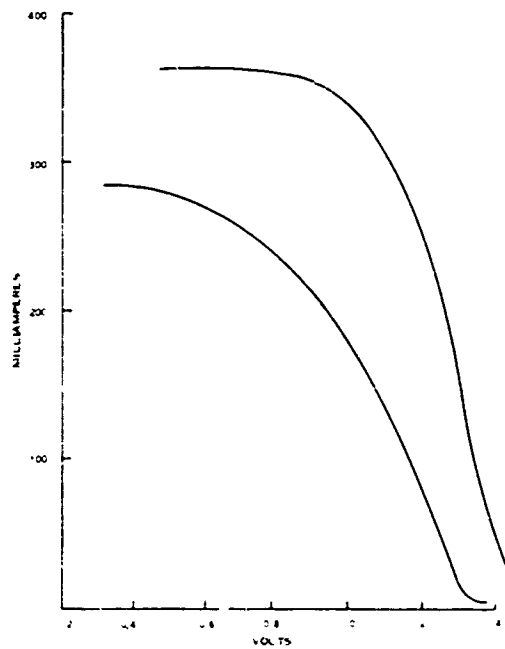
Figure 28. The effect of glassivation on the I-V characteristics of
modules fabricated with N/P solar cells, silver titanium
contacts. (A) Module No. 2; (B), Module No. 3;
(C) Module No. 4.

IX. CONCLUSIONS AND RECOMMENDATIONS

The work demonstrated that:

1. Compositions can be modified so that the resultant glasses have low fusion temperature, relatively low thermal expansion, and good transmission in the wavelength range from 0.25 to 1.2 microns, before and after electron irradiation.

2. These glasses, when crushed to -200 mesh particles and sedimented onto a silicon solar cell, can be fused to the cell surface to form an integral cover.

3. Conventional N/P silver/titanium-contacted silicon solar cells were integrally covered without degrading cell performance. However, the temperature sensitivity of the aluminum-contacted cells resulted in complete degradation of the P/N lithium-doped variety and in only marginal success with the N/P type cells.

4. The sedimented particle/fusion method produces 2.0 mil thick integral covers in much less time than any of the covering techniques being currently evaluated.

While the program yielded several positive results, we believe that the problems defined could be resolved with the following additional effort:

1. A limited continuation of glass development aimed specifically at lowering both fusion temperature and thermal expansion. This would result in successfully covering aluminum-contacted cells

and would allow thicker than 2.0 mil covers to be applied to all types of cells.

2. Optimization of an integral cover application method which maintains the solar cell at a significantly lower temperature while the sedimented glass particles are quickly fused by either a flame fusion or concentrated radiant heat technique.

X. REFERENCES

1. "Final Report - Development of an Integrated Lightweight Flexible Silicon Solar Cell Array", JPL Contract 952560.

2. "Second Topical Report - Space Station Solar Array Technology Evaluation Program ", LMSC-A995719, November 1971.

3. Brackley, C. et al, "Development of Integral Covers for Silicon Solar Cells," Contractor Report, ESRO-CR-68, November 1972.

4. Iles, Peter A., U.S. Patent 3,437,527, April 8, 1969.

5. Enright, D. P., et al, J. Am. Ceram. Soc. 32 (11) 351 (1949).

6. Yee, T. B., et al, J. Am. Ceram. Soc. 38 (12) 378 (1955).

7. Hirayama, C. and Camp, F. E., Glass Tech. 10 (5) 123 (1969).

8. Rawson, H., Inorganic Glass-Forming Systems, Academic Press, New York, 1967, 317 pp.

9. Khalitev, V. D., et al, Opt-Mekli. Prom, 36 (8) 69 (1969).

10. Urusovskaya, L. N., Ah. Prikl. Klim, Leningrad, 41 (11) 2361 (1968).

11. Kingery, W. D., "Surface Tension of Some Liquid Ox ides and Their Temperature Coefficients," J. Am. Ceram. Soc. 42 (1) 6-10, 1959.

12. Weyl, W. A. and Marboe, E. C., The Constitution of Glasses. A Dynamic Interpretation. Vol. II. Constitution and Properties of Some Representative Glasses, Part 1, p. 581 Intersciences Publishers, New York 1964.

13. Sun, K. and Kreidl, N. J., "Coloration of Glass by Radiation, Part II," The Glass Industry, 33, (11) 593 (1952).

14. Monk, G. S., "Coloration of Optical Materials by High Energy Radiation," Report ANL 4536, July 31, 1950.

15. Kreidl, N. J. and Hensler, J. R., "Special Glasses for Nuclear Engineering Applications," in Modern Materials: Advances in Development and Application, Vol. I, Academic Press, New Yor, 402 pp., 1958.

References (cont'd)

16. Bishay, A. M., "Role of Cerium in Suppression of Gamma-Ray Induced Coloring of Borate Glasses," J. Am. Ceram. Soc. 45 (8) 389-393, 1962.

17. Haynes, G. A., "Effect of Radiation on Cerium-Doped Solar-Cell Cover Glass," NASA-Langley Res. Center, Rpt. TN D-6029, December 1970.

18. Barber, R. S. and Richardson, D. A., "Effect of Gamma Radiation on Spectral Transmissions of Some Commercial Glasses," J. Am. Ceram. Soc. 44 (11) 552-560 (1961).

19. Kreidl, N. J., "Interaction Between High Energy Radiation of Glasses," in Ceramics in Severe Environments edited by W. W. Kriegel and H. Palmour III, Plenum Press, New York 1971.

20. Paul, A. and Douglas, R. W., "Cerous-Ceric Equilibrium in Binary Alkali Borate and Alkali Silicate Glasses," Phys. Chem. Glasses 6 (6) 212-215, 1965.

21. Stroud, J.S., "Color-Center Kinetics in Cerium-Containing Glass," J. Phys. Chem. 43 (7) 2442-2450, 1965.

XI. BIBLIOGRAPHY

Spacecraft Solar Cell Arrays, NASA SP-8074, May 1971.

Solar Cell Integral Cover - Glass Development, Final Report,
NAS 5-10319, Texas Instruments Incorporated, Components Group,
February 1967-November 30, 1968.

Kirkpatrick, A. R., et al, "Solar Cell Cover Glass Development,"
Final Report, NAS 5-10236, Ion Physics Corporation, March 1971.

Stella, P. and Somberg, H., "Development of Integral Covers on
Solar Cells," Final Report, NAS 5-21510, Heliotek Division of
Textron, Inc., July 1971.

Somberg, H., et al, "Manufacturing Methods for Silicon Solar Cells
with Integral Coverslips," Technical Report AFML-TR-72-81,
July 1972.

Solar Cells, Proceedings of the International Colloquium July 6-10, 1970,
Toulouse, France, European Cooperation Space Environment Committee,
Gordon and Breach Science Publishers Ltd., London.